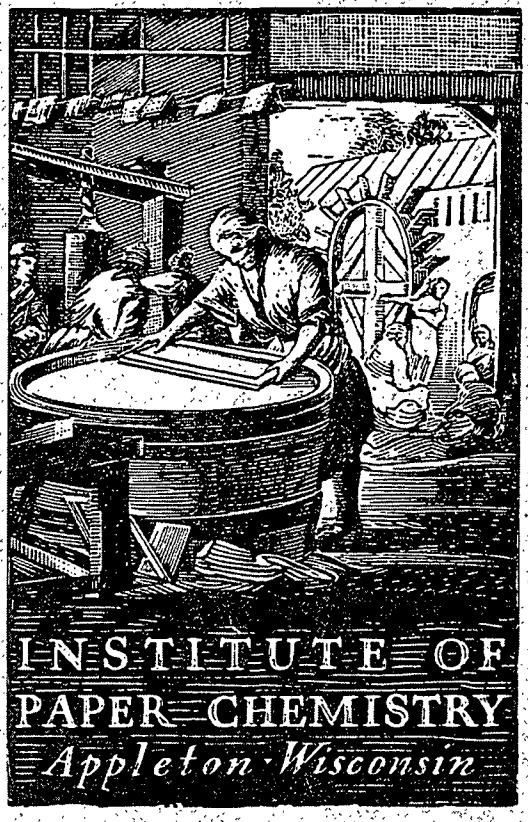

A SURVEY OF EVAPORATOR SCALING IN THE ALKALINE PULP INDUSTRY

Project 3234

Report One

A Progress Report

to

MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

September 22, 1975

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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SUMMARY

A survey of evaporator scaling problems in the alkaline pulp industry was carried out as part of a research program on evaporator scaling. The objectives of the survey were to define the nature and extent of the problem and to identify the most influential variables. Information was obtained by questionnaire and by chemical analysis of the composition of liquor samples which were also submitted.

Calculated values of the average heat transfer coefficient for the evaporation systems of the reporting mills varied from 130 to over 300 Btu/hr/ft^2/°F. This represents a more than two-to-one range in the effective evaporative capacity of a given amount of evaporator surface area. Scaling appears to be the factor primarily responsible for this variability in productivity.

The most commonly reported scales were calcium scales and soluble Na_2CO_3-Na_2SO_4 scales. Calcium scales appear to constitute a more serious problem in the industry. In addition to being more difficult to remove, they can have a dominant effect on evaporator productivity. The data obtained in this survey do not support the concept that rapid growing but easily removable soluble scales are responsible for most of the short-term degradation in evaporator performance while residual, insoluble calcium scales cause only a gradual deterioration in the base-line performance. They indicate, instead, that substantial amounts of calcium scale can be removed by boiling out the evaporator with water, and that rapid growing calcium scales can govern the short-term performance.

The calcium content of the liquor is the most important variable affecting calcium scaling. There are indications that the amount of calcium in the liquor is influenced more by wood supply than by internal process conditions. Parameters controlling the formation of soluble scale could not be identified. No correlations could be established between scaling behavior and those variables associated with the solubility of Na_2CO_3 and Na_2SO_4 in black liquor. This is due in part to the dominance of calcium scales.

The data suggest that some soap in the liquor is beneficial and that there may be an optimum degree of removal. A beneficial effect of residual active alkali in the liquor was also indicated. No correlation could be established between the measured fiber content of the liquor and scaling.

INTRODUCTION

A survey of evaporator scaling problems in the alkaline pulp industry has been carried out. The purpose of the survey was to obtain information on the types and severity of evaporator scaling problems encountered in the industry and to correlate this behavior with liquor composition variables and operating practices. It was intended to complement an on-going experimental study of evaporator scaling.

The first objective of the survey was a definition of the nature and extent of the problem in the industry. Information on the relative prevalence of different types of scales and the extent that they affect evaporator performance was obtained and used to categorize the various scaling problems and assess their general severity.

The second objective was identification of the most influential variables. Evaporator scaling problems are not universally encountered in kraft mills, and these differences in experience must be reflections of differences in liquor composition and operating practice. Cross-correlation analysis of the data obtained in the survey was used to determine the most significant variables. The determination of those variables having the greatest effect on scaling is important in developing concepts regarding scaling mechanisms and rate controlling steps, and is an aid in the selection of parameters for study in the experimental program.

The third objective was knowledge of the range of variables and operating conditions encountered in practice. This helps to establish the normal or typical practice and the extent of variability. An important aspect of this study was the analysis of the composition of a large number of liquor samples to provide a new data base for inorganic constituents in black liquor.

The fourth objective was to set evaporator variables in the context of the entire mill and chemical recovery operations. This permits the examination of relationships between broad mill practices and evaporator performance, and can help to pinpoint some of the ultimate sources of scaling problems. Such information could serve as a starting point for the development of solutions to these problems.

A questionnaire (shown in Appendix I) was used to obtain information on process conditions, evaporator configurations and performance, and types of scales encountered. Samples of black liquor were also requested for subsequent analysis of composition. No attempt was made to obtain blanket coverage of the industry. Twelve companies (including large and small ones) were selected based on the response of those attending the preliminary meeting on this project. Copies of the questionnaire were sent to one representative in each company. A total of 57 questionnaires were sent out.

Forty-eight completed questionnaires were received. Of these, 29 included liquor samples. The completed questionnaires were coded and the data summarized on a uniform basis. Liquor samples were analyzed for the major inorganic substances, residual soap, fiber, and trace metals.

A breakdown of the responses by the pulping process employed is given in Table I. The geographical location of the responding mills is given in Table II.

Response to some of the questionnaires was not as complete as had been hoped. This was especially true with the sections on evaporator performance, cleaning frequencies, and scaling experience. Some of this was apparently due to the choice of wording of the questionnaire. In the majority of cases, sufficient information was given to permit a reasonable estimation of performance parameters.

In general, mills not encountering serious scaling problems tended to give less informative replies.

TABLE I

RESPONSE TO SURVEY

Pulping Process Employed	Completed Questionnaires[a]	Liquor Samples
Kraft	37 (27)	22 (14)
Kraft + semichemical (cross recovery)	7 (4)	4 (3)
Soda	2 (2)	2 (2)
NSSC	2	1

[a] Numbers in parentheses are number of mills doing some bleaching.

TABLE II

GEOGRAPHICAL SUMMARY

Location	Completed Questionnaires	Liquor Samples
South	20	10
Southeast	9	7
East central	4	4
Northeast	4	2
North central	3	1
Northwest	8	5

SURVEY DATA

The data obtained from the survey questionnaires and liquor analyses are summarized in Tables III-XI. These include data on evaporator scaling, evaporator performance, descriptions of evaporator systems, black liquor composition, wood supply, pulping conditions, and white liquor composition. Each entry represents a reply to a questionnaire. The 28 kraft and soda mills for which liquor samples were received and analyzed are listed first, roughly in the order of severity of their scaling problems. These are followed by the remaining 18 kraft mills, also ranked according to severity. The two NSSC mills are listed last.

Data indicative of the extent of evaporator scaling in these mills are presented in Table III. The parameters which are included are the frequencies of water washing, acid cleaning and mechanically cleaning the evaporators, the extent of the loss in evaporation rate in the period between cleanings, and the rate of decline in production capacity. The latter quantity is the product of the percentage decline in evaporation rate per cycle and the sum of the cleaning frequencies. A summary of the types of scale reported and the location of the scale is also given. Blanks in the table indicate that the data were not available.

Although none of the parameters in Table III are direct measures of the rate of scale deposition, they were considered the best available indicators which could be treated quantitatively. The rate of decline in evaporation rate would seem to be most directly related to scaling rate. However, it does not take into account changes in the overall temperature driving force over the evaporators to maintain evaporation rates as scaling proceeds. The rate of decline in the average heat transfer coefficient would be a better measure of scaling, since it also would

TABLE III

DATA ON EVAPORATOR SCALING

Mill No.	Water Wash (Boil Out) Frequency, times/mo.	Acid Cleaning Frequency, times/mo.	Mechanical Cleaning Frequency, times/mo.	Production Loss Between Cleanings, %	Rate of Production Decline, %/mo.	Reported Scale
1	12	3.5	0	7.0	109	Calcium scale 1C & 1AB
2	15	1.15	0	6.5	105	Calcium carbonate, last effect scale greatest
3	7.5	0.17	0.17	30.9	241	Calcium carbonate 87%
4	2.45	2.2	0.03	26.4	124	Calcium and carbonate-sulfate scale, first effects
5	9	0	0.21	15.2	140	$CaCO_3$, 75%. 1A, 1B & 2 effects
6	6	0.67	0	--	--	Carbonate-sulfate scale, aluminum silicate scale, 1A, 1B, 2 & 3 effects
7	8.6	0.03	0.02	--	--	Calcium & silica scale. 60% CaO, 20% SiO_2, 1, 2, 3 & 4 effects
8	5	0.04	0.04	19.0	96.5	Na_2CO_3-Na_2SO_4 scale, 75%
9	5	0.06	0.17	--	--	Calcium carbonate and fiber 2B effect
10	4	0.03	0	22.1	89	Carbonate-sulfate scale and organic 2 effect starts to scale first
11	5.45	0	0.08	2.7	15	Carbonate-sulfate scale, 3 body
12	2	0	0.08	27.4	57	Fiber, Fe & alumina. Most scale can be removed by water washing. 1 & 2 bodies
13	1.33	0	0.17	24	36	Carbonate-sulfate, calcium, & fiber-dried liquor. Bottom of 1 effect
14	3.75	0.04	0.17	--	--	No composition. 1 & 2 effects, more toward top
15	0.8	--	--	10	8	Carbonate-sulfate, calcium, silica & aluminum silicate scale
16	1.6	0.04	0.04	14.8	25	Calcium carbonate. Not having an abnormal scaling problem
17	4	0.08	0.08	4.6	19	No information on scale. "We know of no scale problems"
18	3.5	0	0.02	--	--	Silica. Primary scale buildup is considered to be organic. 1 effect
19	2	0	0	--	--	Calcium scale, some silica. 1 effect
20	1	0.01	0	--	--	Na_2CO_3-Na_2SO_4 scale, no analysis, water washable. 1, 2 & 3 effects
21	0.57	0	0.055	--	--	Carbonate-sulfate & calcium scale. 2 & 3 effects, full tube length
22	0.8	0.11	0	--	--	Carbonate-sulfate scale, from appearance 1 & 3 effects
23	1.5	0.017	0.017	22.8	35	Composition not available. 3, 4 & 5 effects
24	1	0.02	0.08	20.2	22	No known scale
25	--	--	--	--	--	Scaling not a problem at this time
26	1.2	0	0	--	--	No scaling problems
27	0.8	0	0	--	--	Slight but insignificant scale in final pass of 1 effect
28	0.33	0	0	--	--	Only vapor side scale
29	6.5	0.3	--	--	--	Calcium scale primary, carbonate-sulfate secondary
30	6	0	0.04	21.4	129	Aluminum silicate scale. 1B, 1A, 2 & 3 effects
31	4.7	0	0.08	17.8	85	Carbonate-sulfate scale, worse in hot effects
32	--	--	--	--	--	$CaCO_3$ scale, up to 40% fiber
33	15	0	0	--	--	Calcium & sodium scale. Bottom of 2 effect (highest solids)
34	4	0.033	0	26.9	108	Reports silica but analysis suggests $CaCO_3$, Na_2CO_3 & Na_2SO_4, 1 & 2 effects
35	5	0.055	0.016	8.2	42	Scaling not a problem. Primarily in 1 & 2 effects but some in all
36	4	1.33	0	4.7	25	Carbonate-sulfate, calcium & silica scale. 1, 2 & 3 effects, top third, not a major problem
37	4	0.17	--	6.1	25	Carbonate-sulfate. Found in all bodies except feed bodies, increases with temperature
38	3.3	0.02	0.08	--	--	Ligneous carbonate with some Ca and Mg
39	4	0	0.04	10	40	Mild carbonate-sulfate scale. No current problems
40	1	0.17	0	--	--	Carbonate-sulfate, $CaCO_3$ & $MgCO_3$. 1, 2 & 3 effects
41	--	--	--	--	--	$CaCO_3$, slight scaling in all effects. Does not cause operating problems
42	4	0	0	--	--	No scale
43	4	--	--	--	--	No information
44	2	0	0.033	--	--	No scale problem encountered since start up
45	1	0.03	--	--	--	No scale internally
46	1	0	0	--	--	No scale
47	0.83	0.02	0.25	--	--	Carbonate-sulfate, fiber, liquor solids, 1 effect
48	1	0.17	0.8[a]	--	--	Calcium oxalate & carbonate

[a] Caustic boil out.

account for changes in driving force. However, only 12 of the mills provided the necessary data, so it is not included in Table III. The best measure of scaling would be values of the heat transfer coefficients for individual effects as functions of time. These data were not sought because it was felt that they were not readily available and would inhibit the response to the survey.

Data characterizing the operation of the evaporators are presented in Table IV. These include discharge liquor solids content, average heat flux, average thermal driving force, average heat transfer coefficient, steam supply temperature and the ratio of the average evaporation rate to the design rate. These quantities were calculated from reported information on evaporation rates, evaporator geometry, thermal driving forces and liquor solids contents. The value for the solids content of the liquor being discharged from the evaporator is taken prior to the flash tank. The average heat flux is the heat transfer rate per unit heat transfer area for the entire evaporator system. It was calculated as the total heat load (determined from the evaporation rate and including both sensible and latent heat requirements) divided by the heat transfer area. For those mills with more than one set of evaporators, the value presented in Table IV is averaged over all of the sets for which data were reported. The average thermal driving force was calculated from the following equation:

$$\overline{\Delta T} = \frac{(T_{steam} - T_{condenser} - \Sigma \text{ boiling point rise})}{\text{Number of Effects}}$$

If sufficient data were not available, the sum of the boiling point rises was estimated from the reported liquor solids contents. The average heat transfer coefficient was calculated as the average heat flux divided by the thermal driving force. It is the parameter that best characterizes the thermal performance of the evaporators. The saturation temperature of the steam is also included in Table IV

TABLE IV

EVAPORATOR OPERATING DATA

Mill No.	Discharge Liquor Solids Content, %	Average Heat Flux, Btu/hr/ft^2	Average Thermal Driving Force, °F	Average Heat Transfer Coefficient, Btu/hr/ft^2/°F	Saturation Temperature of Steam Supply, °F	Production Ratio, actual/design
1	42	4390	27	163	292	0.93
2	50	3800	30	127	270	0.94
3	46	4330	25.2	172	281	0.82
4	46.9	3690	25	148	281	0.94
5	44.2	2500	17.8	140	280	0.85
6	50	3310	20.4	162	290	--
7	52	3290	22	150	--	--
8	50	3270	24.8	132	312	0.915
9	45	5530	35.5	155	292	1.00
10	49.2	5350	20.3	264	280	1.22
11	57	5890	29	203	270	0.90
12	48	5300	20	265	288	1.12
13	52	--	19.8	--	--	0.92
14	50.6	3640	19	192	280	0.87
15	50	--	22.5	--	298	--
16	46.5	4500	25	180	280	0.85
17	44	6000	23	261	--	0.80
18	43	4430	26	170	310	1.00
19	54	4210	23	184	300	0.97
20	51	4270	17.8	240	281	0.96
21	50	4630	22.2	208	296	0.82
22	48	4320	19.4	223	281	1.0
23	50	4040	19	212	--	0.91
24	50	3910	18.4	213	287	0.95
25	47	--	--	--	--	0.92
26	45	5480	16.7	329	260	1.00
27	50	3770	20.3	186	285	1.00
28	53	3920	20	194	--	0.95
29	50	--	25	--	280	--
30	50	3620	21.8	166	300	0.89
31	45	5700	23.4	243	280	1.25
32	53	--	--	--	--	1.05
33	62	6000	42	143	324	1.35
34	44	5180	19	273	275	1.06
35	45	--	22.5	--	290	0.86
36	44	4040	17.5	231	280	0.93
37	45	--	--	--	300	0.92
38	49.6	5500	19	290	280	1.10
39	47	4940	23	215	296	1.37
40	48.9	--	22	--	293	0.98
41	47	6920	26	276	280	0.94
42	45	--	19.3	--	280	0.6
43	50	6250	33.8	185	280	1.0
44	50	5050	21	241	281	1.01
45	46	4950	23	215	265	--
46	50	--	17	--	260	1.58
47	33	8780	44	200	291	0.65
48	25	--	--	--	--	--

because it has been reported to have an influence on scaling. The production ratio was calculated from the reported average evaporation rate and the design evaporation rate. It is the best estimate that could be made from the available data on the relationship of actual performance to design.

Descriptions of the evaporation systems used are given in Table V. For mills with more than one set of evaporators, separate descriptions are given for each set. All evaporators are straight LTV evaporators unless otherwise noted. Effects are numbered based on steam (or vapor) flows, starting from the highest pressure (all No. 1 effects are fed live steam). Liquor flows are designated in the sequence column with the feed effects at the left and discharge at the right. When two letters are used side by side (e.g., 1AB) it indicates two separate passes in a single body. The letter S is used in the sequence column to indicate the location of the soap skimming operation. Evaporator materials of construction are not included in the table. Type 304 stainless steel is almost universally used for tubes in the higher solids effects and is very common in all effects. Tube diameters are 2 inches unless otherwise noted.

Data on black liquor composition, obtained by analysis of liquor samples which were returned along with the questionnaires, are presented in Tables VI and VII. This unique set of composition data for a large number of industrial black liquors is considered one of the most valuable aspects of this survey. It serves as a reference data base with which any given mill can compare its own liquor, as well as permitting correlation of liquor composition variables with scaling behavior.

Weight percentages of liquor components which were considered most likely to influence scaling behavior are given in Table VI. All composition

TABLE V

EVAPORATOR DESCRIPTIONS

Mill No.	Set	Bodies	Effects	Average Tube Length, ft	Heat Transfer Area, ft^2	Sequence	Comments
1	1	8	5	26.4	40,700	5-4-4C-3C-3-2-1C-1AB	After heaters on 5, 4, 3, & 2. Do not skim soap
2	1	5	4	22	35,600	--	Normally one body out for maintenance. No. 1 effect 2-pass
	2	3	3	14	6,000	--	--
3	1	6	5	20-26	55,000	5>4 3-S-2-1C-1B	3 Liquor passes in 1C & 1B
	2	7	6	--	--	6>5 4-5-3-2-1B-1A	Internal preheat in 2. 2 Passes in 1B & 1A
4	1	7	5	22	25,600	5-4-S-3-2B-2A-1B-1A	--
	2	6	5	22	47,700	5-4-3-S-2-1B-1A	--
	3	6	5	22	51,300	5>4 3-S-2-1C-1AB	--
	4	6	5	22	58,900	4-5 3-S-2-1C-1AB	--
5	1	7	6	24	72,400	5—4 6 3-2-1B-1A	Soap skimmer location not defined
	2	6	6	28	120,000	5>6 4-S-3-2-1AB	--
	3	7	7	28	144,000	6>7 5-4-S-3-2-1AB	After heaters on 7, 6, 5, 4, 3, 2. Preheater on 1B
6	1	6	6	28	90,000	6>5 4-S-3-2-1AB	Takes 2/3 of feed
	2	8	7	24	73,000	7>6 5-4-S-3-2-1A-1B	Takes 1/3 of feed
7	1	5	5	22	15,900	5>4 3-S-2-1	--
	2	5	5	20	22,000	5>4 3-S-2-1	--
	3	6	6	22	38,900	6>5 4-S-3-2-1	--
	4	6	6	22	29,000	6>5 4-S-3-2-1	--
	5	6	6	28	56,000	6>5 4-S-3-2-1AB	--
8	1	6	6	--	--	6>5 4-S-3-2-1AB	--
	2	6	6	24	127,200	6>5 4-3-S-2AB-1AB	Afterheaters on 6, 5, 4, 3. Internal preheat in 2AB
9	1	4	4	28	81,800	3-4-S-2-1AB	After heaters on 2, 3 & 4
10	1	7	6	24	94,800	6>5 4-S-3-2-1A-1B	Afterheater in 5 for feed to 4
11	1	5	4	28	112,600	3-4-S-2-1B-1A	Internal preheat in original design has been removed
12	1	7	6	20	48,400	5-6-4-S-3-2-1C-1AB	Afterheater on 6. 60% feed 5 and 40% to 4
	2	6	6	26	47,300	5-6-4-S-3-2-1AB	Afterheater on 6. 60% feed 5 and 40% to 4
13	1	6	5	--	--	5>4 3-S-2-1B-1A	--
	2	6	5	--	--	5>4 3-S-2-1B-1A	--
	3	6	6	26	--	5>6 4-S-3-2-1AB	1-1/4-Inch tube diameter. Afterheaters on 2, 3, 4, 5, & 6
	4	6	6	26	--	5-6-4-S-3-2AB-1ABC	1-1/4-Inch diameter tubes. Afterheaters on 3, 4, 5, & 6. No. 1 effect LTV & PFR. Feeds 2 concn.

TABLE V (Continued)

EVAPORATOR DESCRIPTIONS

Mill No.	Set	Bodies	Effects	Average Tube Length, ft	Heat Transfer Area, ft^2	Sequence	Comments
14	1	6	6	28	131,000	5-6-4-S-3-2-1AB	Afterheaters on 2, 5 & 6
15	1	6	6	30	--	5-6-4-3-2-1AB	Soap removal at washers, weak tank & between No. 1 & 2 for all six sets
	2	7	7	30	--	6,7>5-4-3-2-1AB	
	3	7	7	30	--	6,7>5-4-3-2-1AB	--
	4	7	7	30	--	6-7-5-4-3-2-1AB	--
	5	7	7	30	--	6-7-5-4-3-2-1AB	Inverted first effect. Liquor & vapor flow down
	6	7	7	30	--	6-7-5-4-3-2-1AB	--
16	1	6	5	28	113,000	4-5,3>S-2-1B-1A	Afterheaters on all but 1A
17	1	6	5	24.8	37,400	4,5>S-3-2-1B-1A	1-5/8-Inch tubes in 1A
	2	6	6	26	64,500	6,5>S-4-3AB-2AB-1AB	--
	3	6	6	26	86,400	6AB,5AB>S-4AB-3AB-2AB-1AB	--
	4	4	4	28	34,000	3-4-1-2	Used as a feed sweetener
18	1	6	6	22	43,600	6,5>4-S-3-2-1	--
	2	6	6	22	43,600	6,5>4-S-3-2-1	--
19	1	6	5	22	31,100	4,5>3-2-1B-1A	Soap not removed
	2	6	6	22	37,250	5,6>4-3-2-1AB	--
	3	6	6	22	37,250	5,6>4-3-2-1AB	--
	4	6	6	22	36,750	5,6>4-3-2-1AB	--
20	1	5	5	24	22,960	4,5>3-S-2-1AB	Internal preheat 1, 2 & 3
	2	5	5	26.5	22,800	4,5>3-S-2-1AB	Internal preheat 1, 2 & 3
	3	5	5	28	22,800	4,5>3-S-2-1AB	Internal preheat 1, 2 & 3
	4	7	7	28	117,500	6-7-4-S-3-2-1AB, 5	Afterheaters 2, 3, 4, 6 & 7
	5	7	7	28	140,000	6-7-4-S-3-2-1AB, 5	Afterheaters 2, 3, 4, 6 & 7
21	1	7	6	22	37,400	6,5>4-3-1-2B-2A	Soap skimmed from weak liquor. Heat exch. with cond. from 1
22	1	6	6	30	126,000	5-6-4-3-2-1	Feeds a concentrator. All have internal preheaters
23	1	6	6	22	65,500	6,5>4-S-3-2-1AB	--
	2	6	6	22	65,500	6,5>4-S-3-2-1AB	--
24	1	6	6	26	77,700	5-6-4-3-2-1AB	Feeds concentrator. No. 2 is 3-pass. No. 1 is falling film. Int. pre-heat 2-6
25	1	7	6	24	--	Feed 5 & 6	No soap skimming. Internal preheater
	2	3	3	24	--	--	No. 1 & 2 are PFR concentrators, No. 3 is preevap. for set 1
26	1	6	6	28	80,800	5-6-4-S-3-2-1AB	Afterheaters on 2, 3, 4, 5, 6
27	1	6	6	28	140,300	5-6-4-S-3-2-1AB	Internal heaters not used
28	1	6	6	24	90,000	5,6>4-3-2-1AB	Internal preheat. No soap removal
	2	6	6	24	83,400	5,6>4-3-2-1AB	Internal preheat. No soap. Part feeds a concn.

TABLE V (Continued)

EVAPORATOR DESCRIPTIONS

Mill No.	Set	Bodies	Effects	Average Tube Length, ft	Heat Transfer Area, ft^2	Sequence	Comments
29	1	7	6	32	72,000	Feed 5 & 6	Soap removal not specified
	2	5	4	24	47,500	--	Has postheaters
30	1	6	5	25.3	183,300	5,4>3-S-2-1B-1A	Feed concentrator
	2	7	6			5-6-4-S-3-2-1B-1A	Internal preheat & reheat. Feed concentrator
31	1	7	6	24	57,300	5,6>S-4-3-2-1B-1A	Sweeten feed
	2	6	5	24	45,300	5,6>S-4-3-2-1AB	Sweeten feed
	3	6	5	24	63,200	5,6>S-4-3-2-1AB	Sweeten feed
32	1	6	5	--	--	4,5>S-3-2C-2AB-1AB	Afterheaters 4, 5, 3, 2C. Preheat & afterheat 2AB & 1AB
33	1	4	4	28	97,300	3-4-S-1-2AB	3 External preheaters before No. 1
34	1	7	6	24.4	62,800	5,6>S-4-3-2-1B-1A	
	2	6	5	21	81,600	5-6-S-4-3-2-1AB	Afterheater on 6
	3	6	5	24	57,700	5-6-S-4-3-2-1AB	Afterheater on 5 & 6. Internal preheat 4, 3, 2, 1A
35	1	7	6	27	--	5-6-4-S-3-2-1C-1AB	Sweeten feed, 2/3-5 & 1/3-4. Afterheater on 6. Ext. heater to & from soap
	2	6	6	27	--	5-6-4-S-3-2-1	Sweeten feed, 2/3-5 & 1/3-4. Afterheater 2, 3, 4, 5 & 6. Preheaters on 1
36	1	6	6	32	85,300	6,5>4-S-3-2-1	--
	2	6	6	28	85,300	6,5>4-S-3-2-1	--
37	1-3	--	--	--	--	--	--
38	1	7	6	28	97,700	6,5>4-S-3-2-1C-1AB	Afterheaters 2-6. Part to concentrator
	2	6	6	28	141,200	6,5>4-S-3-2-1AB	Afterheaters 2-6. Part to concentrator
39	1	7	6	32	66,000	--	--
40	1	7	6	24	--	5-6-4-3-2-1A-1B	No soap removal. Internal preheaters 2,3,5 & 6
41	1	6	5	24	40,800	4-5-3-S-2-1C-1AB	68% to 4 & 32% to 3
	2	7	5	24	--	4-5-3-S-2B-2A-1B-1A	1-1/2 Inch x 14 ft tubes in 1A. 60% to 4 & 40% to 3. 2 pass in No. 5
42	1	6	5	--	22,500	5-4-3-2-1B-1A	No soap removal
	2	5	5	--	18,500	5-4-3-2-1AB	No soap removal
	3	5	5	--	18,500	5-4-3-2-1AB	No soap removal
	4	7	7	28	107,000	6,7>5-4-3-2AB-1AB	No soap removal. Feeds conc. Afterheaters 3-7. Waste heat evaporators 6A & 7A
43	1	4	4	26	45,500	4-S-3-2-1AB	Feeds concentrator. After heaters in 2, 3 & 4
44	1	6	6	28	114,500	5-6-S-3-2-1AB (4)	Internal preheat 2-6
45	1	9	5	28	82,200	6,5>4-S-3B-3A-2B-2A-1B-1A	1A & 1B each 2-pass. No. 1A tubes 23.5 ft
46	1	6	6	28	--	--	--
47	1	4	3	9.7	7,400	2A,2B>3-1	7/8-inch diameter tube. 4-Pass heater before No. 1. Forced circulation evaps.
48	1	7	6	25	--	5-6-4-3-2-1BC-1A	Internal preheat 1BC
	2	4	4	25	--	3,4>2-1	Forced circulation

TABLE VI

BLACK LIQUOR COMPOSITION DATA

(Expressed as wt.% on liquor solids)

Mill No.	Na_2CO_3	Na_2SO_4	Residual Active Alkali (as Na_2O)	Total Sodium	Calcium	Potassium	Residual Soap	Fiber	Critical Solids Content, %
1	8.3	1.5	4.8	17.2	0.108	2.4	0.32	0.021	56.1
2	10.5	1.0	6.35	19.6	0.102	0.88	0.47	0.052	51.9
3	10.7	4.3	5.45	19.4	0.069	1.0	0.97	0.029	49.6
4	9.1	2.6	6.5	18.6	0.030	0.93	0.55	0.022	53.2
5	6.8	2.6	5.9	17.2	0.073	2.7	0.76	0.029	56.3
6	10.3	4.1	4.25	18.9	0.017	0.80	0.58	0.028	51.4
7	8.3	4.3	6.3	18.9	0.033	1.0	0.55	0.029	52.1
8	7.5	3.8	6.0	18.0	0.045	0.92	1.41	0.014	54.2
9	9.9	5.8	5.8	19.6	0.055	2.5	0.55	0.007	49.2
10	9.9	2.9	5.0	18.7	0.017	1.0	1.87	0.159	52.5
11	12.3	3.2	7.75	20.5	0.021	1.4	0.96	0.080	49.1
12	9.4	2.2	6.0	18.7	0.012	1.8	0.56	0.014	53.2
13	7.1	2.3	5.3	17.3	0.017	1.2	1.02	0.016	56.3
14	6.9	8.3	6.0	19.8	0.025	1.1	0.43	0.001	48.4
15	8.4	4.6	6.8	18.4	0.028	1.2	1.14	0.049	52.3
16	9.0	1.6	6.25	17.9	0.025	1.5	1.48	0.007	54.6
17	9.6	4.6	4.9	19.3	0.018	1.5	0.90	0.024	50.8
18	7.0	2.5	5.55	17.4	0.027	0.97	0.71	0.026	56.2
19	10.9	3.2	4.05	18.1	0.028	0.88	1.00	0.025	53.1
20	8.7	3.9	7.4	19.4	0.049	2.2	1.62	0.014	51.4
21	8.1	4.5	3.9	18.2	0.023	1.8	1.57	0.021	53.1
22	7.8	3.2	6.05	18.6	0.030	2.1	0.64	0.002	53.5
23	6.7	3.3	6.3	18.6	0.052	1.1	--	--	54.3
24	7.8	0.9	7.3	19.2	0.022	1.6	0.34	0.043	53.4
25	9.1	2.6	5.55	18.0	0.017	0.44	1.39	0.006	54.2
26	8.9	2.8	5.6	18.3	0.009	1.2	0.82	0.005	53.6
27	6.6	2.7	6.85	18.5	0.019	1.2	1.23	0.046	54.7
28	7.3	1.5	8.6	20.5	0.026	0.86	1.33	0.028	51.9
47	0.6	4.5	0.6	16.5	0.062	0.43	0.16	0.094	59.2

TABLE VII

TRACE METAL ANALYSES ON BLACK LIQUORS

(Expressed as ppm on liquor solids)

Mill No.	Boron	Silicon	Manganese	Iron	Magnesium	Aluminum	Vanadium	Calcium	Copper
1	180	1800	94	94	190	140	7	1300	16
2	89	800	110	71	220	120	7	1200	440
3	49	510	73	78	180	220	160	630	7
4	120	1300	96	90	180	73	180	420	36
5	110	1150	120	87	175	96	320	730	60
6	100	1000	140	86	160	300	120	310	22
7	380	1300	70	120	240	220	180	520	38
8	68	670	88	71	170	240	190	340	7
9	180	1500	220	110	240	80	7	770	27
10	140	1600	84	98	160	220	7	310	27
11	680	460	45	100	200	80	420	470	89
12	260	1000	120	95	170	75	7	300	12
13	92	1400	48	98	140	62	220	220	26
14	120	1200	69	100	180	84	7	310	130
15	260	1400	75	110	140	260	30	350	98
16	120	1800	100	100	190	240	7	370	86
17	600	1200	82	110	170	170	600	300	89
18	300	1400	130	80	200	220	32	320	36
19	120	1600	42	89	170	190	7	340	12
20	170	1400	140	120	240	170	170	610	26
21	130	1500	120	88	140	68	120	320	88
22	120	720	100	98	230	42	7	440	87
23	450	630	64	58	170	140	110	380	10
24	100	1000	100	86	160	51	58	220	510
25	100	1400	46	100	150	100	42	260	120
26	260	240	78	56	170	32	7	40	26
27	230	1000	97	93	180	120	68	420	15
28	140	1000	130	79	230	76	7	350	19
47	54	750	280	150	380	37	7	400	72

data (except for critical solids content) are expressed on a dry solids basis. The analytical procedures which were used are discussed in Appendix II. The critical solids content is the liquor solids content at which a particular liquor reaches saturation with respect to Na_2CO_3 and Na_2SO_4. The solubility behavior of Na_2CO_3 and Na_2SO_4 in black liquor and the method of determining the critical solids content are described in Appendix III. Trace metal data, as determined by flame emission spectroscopy, are presented in Table VII. These data are expressed as ppm on the dry liquor solids. They can be converted to weight percent by dividing by 10,000. It should be noted that there are two independent determinations of the calcium content of the liquors. The values in Table VI were obtained by atomic absorption spectroscopy, while those in Table VII are by emission spectroscopy.

Mill process conditions are presented in Tables VIII, IX, and X. Data on wood supply are given in Table VIII. This includes the amount of hardwood, the amount of whole tree chips, wood storage time, and estimates of the degree of bark removal and dirt content. Pulping process conditions are defined in Table IX. Presented are the reported pulp yield, the relative amount of pulp that is bleached, and the amount of semichemical pulp produced by those mills practicing cross recovery. Data on white liquors are given in Table X. These were obtained from the questionnaires and not by analyses of samples. The reported data include the cooking chemical charge (expressed as the amount of effective alkali, as Na_2O, on the o.d. wood), and concentrations of key chemicals in the white liquor.

Various averages of the survey data and indications of the variability are given in Table XI. Included are the arithmetic mean, median and geometric

TABLE VIII

DATA ON WOOD SUPPLY

Mill No.	Hardwood, %	Whole Tree Chips, %	Storage Time, mo.	Bark Removal	Dirt Content
1	100	0	3	Fair	Average
2	98	0	2	Good	Low
3	95	0	2	Fair	High
4	23	0	1	Good	Low
5	38	3	2	Fair	Average
6	20	4.5	5	Fair	High
7	23	10	0.25	Good	Average
8	0	0	2	Fair	High
9	70	0	2	Good	Low
10	10	0	2	Good	Average
11	40	0	8	Good	High
12	45	0	3	Good	Low
13	30	1.3	6	Good	Average
14	5	0	4	Good	Average
15	7	0	1	Good	Average
16	35	0	0.55	Fair	Average
17	38	4	0.25	Fair	Average
18	15	5	9	Fair	High
19	20	3	1	Fair	Average
20	65	5	1	Good	Low
21	75	0	3	Poor	Low
22	80	10	2	Fair-poor	Average
23	4	0	2	Good	High
24	65	0	3	Good	Average
25	5	5	9	Fair	Average
26	15	0	0.5	Fair	Average
27	10	0	1	Good	Average
28	0	0	1.5	Fair	Low
29	70	5	6	Fair	Average
30	15	5	1	Good	Average
31	14	0	6	Good	Average
32	22	17	6	Good	Average
33	1	20	0	Fair	Low
34	23	0	3	Good	Average
35	35	0	1	Fair	Average
36	32	0	1.5	Good-fair	High
37	21	0	1.5	Good	Low
38	10	5	0.67	Good	Low
39	10	0	1	Good	Low
40	25	0	6	Fair	Average
41	42	0	2.5	Fair	Low
42	5	5	2	Good	Low
43	0	0	3	Fair	Average
44	3	0	--	Good	Average
45	8	0	1.5	Good	Low
46	40	0	1	Good	Average
47	100	20	1	Fair	High
48	100	0	6	Poor	Average

TABLE IX

PULPING PROCESS CONDITIONS

Mill No.	Yield, %	Bleached Pulp, % of prodn.	Semichem., % of prodn.
1	45.5	100	0
2	--	100	0
3	53.5	0	0
4	48	40	0
5	49.4	100	0
6	55.5	0	16
7	52.4	40	12
8	53.5	0	0
9	47	100	0
10	55	0	0
11	45	100	0
12	49	100	0
13	47	100	0
14	46	100	0
15	--	19	9
16	--	100	0
17	52	45	0
18	54.5	0	0
19	49.7	76	24
20	48	100	0
21	43.3	100	0
22	48	100	0
23	56.5	0	0
24	40	100	0
25	52	0	0
26	54.4	0	0
27	55	0	0
28	44	100	0
29	45	100	0
30	53	0	14
31	47	37	0
32	45	100	0
33	--	100	0
34	--	22	11
35	47	100	0
36	46	100	0
37	46	60	0
38	51	0	14
39	47.6	100	0
40	43	100	0
41	--	100	0
42	46	0	0
43	55	0	0
44	55	22	0
45	--	--	0
46	44	100	0
47	70	0	100
48	79	0	100

TABLE X

WHITE LIQUOR DATA

Mill No.	Charge Eff. Alkali on o.d. wood, %	Active Alkali, g Na_2O/l	Na_2S g Na_2S/l	Na_2CO_3, g Na_2CO_3/l	Na_2SO_4, g Na_2SO_4/l	Calcium, g Ca/l
1	15	118.7	19.2	19.2	0.64	--
2	3.9	380	0.3	1.0	0.5	--
3	13.3	90	29.4	19.5	22.0	0.038
4	16.9	104	38	39	12	--
5	--	90	37	17	7	0.025
6	12.5	98.3	27.2	27.2	9.2	0.096
7	15.8	105.5	42.1	25.2	--	--
8	13.3	90	29.4	19.5	22.0	0.038
9	19.0	105	28.9	25.6	30	0.200
10	14.5	101	28.8	35.3	6.8	0.025
11	16.9	97.6	32.2	35.6	--	0.096
12	11.7	180	80	40	5.5	0.15
13	16.5	131	40	43.2	6.4	--
14	17	102.5	20.2	27.4	18.3	--
15	16.5	97	37.6	25	11.5	--
16	14.1	112	33	37	2.8	--
17	8.3	106	46	46.3	--	0.41
18	11.6	--	--	--	--	--
19	15.8	94.5	28.8	38.4	3.2	0.050
20	16	95.5	27.3	43.6	5.5	0.006
21	14.8	84.8	21.0	9.5	--	--
22	14	99	24	4.8	4.8	0.078
23	16	109	21	11	0.1	0.53
24	15.8	110.5	40	40	--	--
25	14.5	112	40	40	8	0.035
26	12.5	100.4	29.8	37.6	8.6	--
27	12.9	98	48	--	--	--
28	16.9	103	35	30	4.6	0.06
29	15.5	--	--	--	--	--
30	13.5	96	24	--	--	0.075
31	10.5	116	38	--	--	2.7
32	17.5	100.7	43.5	24	10.9	0.06
33	14.5	83	48	43	6.4	0.0004
34	--	109.9	36.9	35.3		0.13
35	--	106.7	27.6	48.2	7.3	--
36	15.5	96	38.5	28.8	2.2	--
37	17.1	108.5	37.2	8.1	5.6	0.01
38	14	98	29	48	--	--
39	17.3	93	27	19	4.8	--
40	14.5	96	29.8	31.4	0.96	--
41	14.5	109.5	47.6	49.4	--	0.7
42	15	96	30	30	--	--
43	--	105.5	28.8	--	--	--
44	12.6	112	44	41	5	0.04
45	15.5	111	50	16	--	0.05
46	17	111.4	38.1	24.8	--	--
47	11.3[a]	163.8[a]	--	42.4	5.5	--
48	7[b]	54.5	20.8	19.2	41.7[a]	--

[a] As Na_2SO_3.

[b] Effective chemical.

TABLE XI

AVERAGES OF SURVEY VARIABLES

Variable	Arithmetic Mean	Arithmetic Standard Deviation	Median	Geometric Mean	Geometric Standard Deviation
Water wash freq., times/mo.	4.09	3.5	4.00	2.82	2.48
Acid cleaning freq., times/mo.	0.25	0.67	0.021	--	--
Mechanical cleaning freq., times/mo.	0.047	0.059	0.017	--	--
Production loss between cleaning, %	15.8	8.6	16.5	13.0	1.99
Rate of production loss, %/mo.	71.6	55.6	49.3	51.6	2.36
Evaporator discharge solids, %	48.6	3.7	49.4	48.5	1.08
Av. heat flux, Btu/hr ft^2	4605	993	4465	4495	1.25
Av. ΔT, %	23.0	5.1	22.1	22.5	1.22
Av. heat transfer coeff., Btu/hr/ft^2/°F	201	52	193	195	1.30
Saturated steam temperature, °F	286	13	281	285	1.05
Production ratio, actual/design	0.985	0.17	0.945	0.97	1.17
Black liquor					
Na_2CO_3, %	8.7	1.45	8.55	8.55	1.18
Na_2SO_4, %	3.2	1.5	3.05	2.9	1.63
Residual active alkali (as Na_2O), %	5.95	1.05	6.0	5.85	1.20
Total sodium, %	18.7	0.88	18.6	18.7	1.05
Calcium, %	0.036	0.025	0.0265	0.029	1.83
Potassium, %	1.36	0.57	1.2	1.26	1.50
Residual soap, %	0.93	0.42	0.90	0.83	1.62
Fiber, %	0.031	0.031	0.025	0.0195	2.90
Critical solids, %	52.9	2.1	53.1	52.8	1.04
Black liquor trace metals					
Boron, ppm	202	153	135	163	1.87
Silicon, %	1140	400	1200	1050	1.58
Manganese, ppm	96	37	96	89	1.46
Iron, ppm	91	16	94	90	1.20
Magnesium, ppm	184	30	178	181	1.17
Aluminum, ppm	139	75	120	118	1.81
Vanadium, ppm	111	141	50	41	4.80
Calcium, ppm	450	270	350	380	1.85
Copper, ppm	77	116	32	39	3.00
Hardwood, %	31	29	22.5	--	--
Whole tree chips, %	2.3	4.3	0	--	--
Storage time, mo.	2.7	2.3	2.0	--	--
White liquor					
Active alkali (as Na_2O), g/liter	110.6	43.6	102.8	106.5	1.26
Na_2S, g/liter	34.1	11.7	32.6	30.1	2.10
Na_2CO_3, g/liter	29.6	12.5	30.0	25.1	2.10
Na_2SO_4, g/liter	8.0	6.9	6.4	5.0	3.30
Calcium, g/liter	0.23	0.54	0.06	0.065	5.40

mean, the ordinary arithmetic standard deviation and a geometric standard deviation of most of the survey parameters. The geometric mean, $\overline{X}_*$, is defined as the Nth root of the product of N pieces of data. Thus,

$$\overline{X}_* = \sqrt[N]{X_1 \cdot X_2 \cdot X_3 \cdot \ldots X_N}$$

or

$$\log \overline{X}_* = \sum_{i=1}^{N} \frac{\log X_i}{N}$$

The arithmetic standard deviation is defined as follows:

$$\text{a.s.d.} = \sqrt{\sum_{i=1}^{N} \frac{(X_i - \overline{X})^2}{N}}$$

where $\overline{X}$ = arithmetic mean. The geometric standard deviation is defined in an analogous manner as follows:

$$\log(\text{g.s.d.}) = \sqrt{\sum_{i=1}^{N} \frac{(\log X_i - \log \overline{X}_*)^2}{N}} = \sqrt{\sum_{i=1}^{N} \frac{(\log X_i/\overline{X}_*)^2}{N}}$$

It is a measure of the spread in the data based on ratios with the mean. A value of the geometric standard deviation of 1 means all data are identical. The higher the number, the greater the spread.

DISCUSSION OF RESULTS

An important feature of the data obtained in the survey is the mill-to-mill variability in scaling experience and evaporator thermal performance. Reported scaling ranged from severe, requiring frequent cleaning of the heat transfer surface, to none at all. Values of the average heat transfer coefficient ranged from about 130 to over 300 Btu/hr/ft^2/°F, a better than two-to-one range in the effective use of evaporator surface area. This variability among apparently similar mills is strong evidence that evaporator scaling can be minimized or eliminated provided the key variables can be identified and controlled.

Because of the large number of mills reporting and the many variables which had to be considered, statistical methods were used to attempt to uncover causal relationships and to determine the most significant parameters. Linear regression equations and correlation coefficients between paired variables were determined for all possible pairs. Scatter diagrams for those pairs exhibiting relatively high correlation coefficients (normally 0.4 or higher) were examined to guard against spurious correlations due to isolated points. The statistical analysis was limited to screening variable pairs. Correlations involving more than two variables at a time were not determined because of the enormous number of combinations involved and the increased likelihood of chance correlations which would complicate the interpretation of the results.

SCALING BEHAVIOR

There are two basic problems which complicate the interpretation of evaporator scaling data.

1. It is not possible to get data on the actual rates of deposition of scale. These must be inferred from the

effect of scaling on evaporator performance, which can be affected by other factors than scaling.

2. Several different types of scale can be depositing simultaneously, and it is difficult to determine the relative extents of the different types.

The five quantities listed in Table III (frequencies of water washing, acid cleaning and mechanically cleaning the evaporator, production loss between cleanings, and the rate of production decline) are variables which are indicative of scaling and which can be assigned numerical values. They are suitable for analysis by the statistical techniques employed. Correlations of these variables with liquor composition and evaporator design and operating variables can be carried out directly.

Problems associated with the determination of the relative prevalence of different types of scale are more difficult to overcome. A breakdown of the types of scales as reported by the 46 kraft and soda mills is given in Table XII.

TABLE XII

TYPES OF SCALE REPORTED

Type of Scale	Number of Mills	Type of Scale	Number of Mills
$CaCO_3$	20	Fiber	3
Na_2CO_3-Na_2SO_4	19	Organic	3
Silica	5	No scale	10
Aluminum silicate	4	No information	3

Many of the mills encountered more than one type of scale. The total scaling experience is then a composite of several processes occurring simultaneously, possibly controlled by entirely different variables. Some types of

deposits are more easily removed than others (for example, by boiling out with water), and often scale analyses are only available for the more insoluble materials which build up over longer times. For this reason the data on scale composition in Table III, must be treated with caution.

No satisfactory method of quantitatively distinguishing the effects of different types of scale was developed. Several approaches were tried, but each was nonobjective and subject to bias. The procedure which was finally adopted was to correlate the five objective parameters discussed previously and use the information on different types of scale in interpreting the results.

Correlation with Liquor Composition

A summary of the correlation coefficients between the data on evaporator scaling in Table III and the liquor composition data in Tables VI and VII is given in Table XIII. The square of the correlation coefficient is a measure of the amount of variation in one paired variable which can be explained by variation in the other. Coefficients indicating a significant degree of correlation between variable pairs are underlined in Table XIII. Spurious correlations are indicated by a parenthesis.

It is evident that the single most important liquor composition variable is the calcium content of the liquor. There are significant correlations between water washing frequency, acid cleaning frequency, and rate of production decline and the calcium content of the liquor as determined by either of the procedures used (the correlation coefficient for one calcium determination against the other is 0.93). The data relevant to these correlations are summarized in Table XIV. Scatter diagrams for water washing frequency, acid cleaning frequency, and rate of production decline versus calcium in the liquor as determined by atomic absorption are given in Fig. 1-3, respectively. Linear regression lines are also shown.

TABLE XIII

CORRELATION OF SCALING EXPERIENCE WITH LIQUOR COMPOSITION

	Water Washing Frequency	Acid Cleaning Frequency	Mechanical Cleaning Frequency	Production Loss Between Cleanings	Rate of Production Decline
Sodium carbonate	0.30	0.10	0.07	0.28	0.12
Sodium sulfate	0.09	0.27	0.39	0.02	0.07
Residual active alkali	0.18	0.15	0.05	0.15	0.37
Total sodium	0.01	0.22	0.01	0.19	0.09
Calcium A.A.	0.78	0.57	0.09	0.24	0.58
Potassium	0.08	0.13	0.35	0.27	0.01
Residual soap	0.43	0.41	0.21	0.11	0.11
Fiber	0.16	0.06	0.20	0.09	0.04
Critical solids content	0.07	0.20	0.20	0.17	0.06
Boron	0.04	0.15	0.08	(0.52)	(0.54)
Silicon	0.02	0.26	0.01	0.11	0.20
Manganese	0.06	0.03	0.06	0.07	0.26
Iron	0.07	0.03	0.14	0.34	(0.43)
Magnesium	0.26	0.04	0.20	0.40	0.29
Aluminum	0.20	0.01	0.25	0.07	0.12
Vanadium	0.12	0.12	0.33	0.33	0.10
Calcium E.S.	0.80	0.63	0.01	(0.41)	0.46
Copper	0.23	0.03	0.03	0.27	0.20
Aluminum x silicon	0.07	0.09	0.31	0.22	0.18

The highest degree of correlation is between the water washing (or boil out) frequency and the calcium content of the liquor. The validity of this correlation is clearly evident in Fig. 1. It is instructive to examine the points furthest removed from the correlation. Those points which are below the regression line constitute mills which have a relatively high calcium content in the liquor without a correspondingly high boil out frequency. Mills 20 and 22 deviate furthest in this direction. It appears that the measured calcium content is too high for Mill 23. This is one of a very few liquors in which the measured calcium by atomic absorption is greater than the value obtained by emission spectroscopy. On the other hand, the data for Mill 20 appear valid. This is the only mill in which the calcium content of the liquor was well above average, and yet the mill

TABLE XIV

EFFECT OF CALCIUM ON SCALING RATE

Mill No.	Water Washing Frequency, times/mo.	Acid Cleaning Frequency, times/mo.	Rate of Production Decline, %/mo.	Atomic Absorption Ca in Liquor, % on solids	Emission Spec. Ca in Liquor, % on solids
1	12	3.5	109	0.108	0.130
2	15	1.15	105	0.102	0.120
3	7.5	0.17	241	0.069	0.063
4	2.45	2.2	124	0.030	0.042
5	9	0	140	0.073	0.073
6	6	0.67	--	0.017	0.031
7	8.6	0.03	--	0.033	0.052
8	5	0.04	96.5	0.045	0.034
9	5	0.06	--	0.055	0.077
10	4	0.03	89	0.017	0.031
11	5.45	0	15	0.021	0.047
12	2	0	57	0.012	0.030
13	1.33	0	36	0.017	0.022
14	3.75	0.04	--	0.025	0.031
15	0.8	--	8	0.028	0.035
16	1.6	0.04	25	0.025	0.037
17	4	0.08	19	0.018	0.030
18	3.5	0	--	0.027	0.032
19	2	0	--	0.028	0.034
20	1	0.01	--	0.049	0.061
21	0.57	0	--	0.023	0.032
22	0.8	0.11	--	0.030	0.044
23	1.5	0.017	35	0.052	0.038
24	1	0.02	22	0.022	0.022
25	--	--	--	0.017	0.026
26	1.2	0	--	0.009	0.004
27	0.8	0	--	0.019	0.042
28	0.33	0	--	0.026	0.035

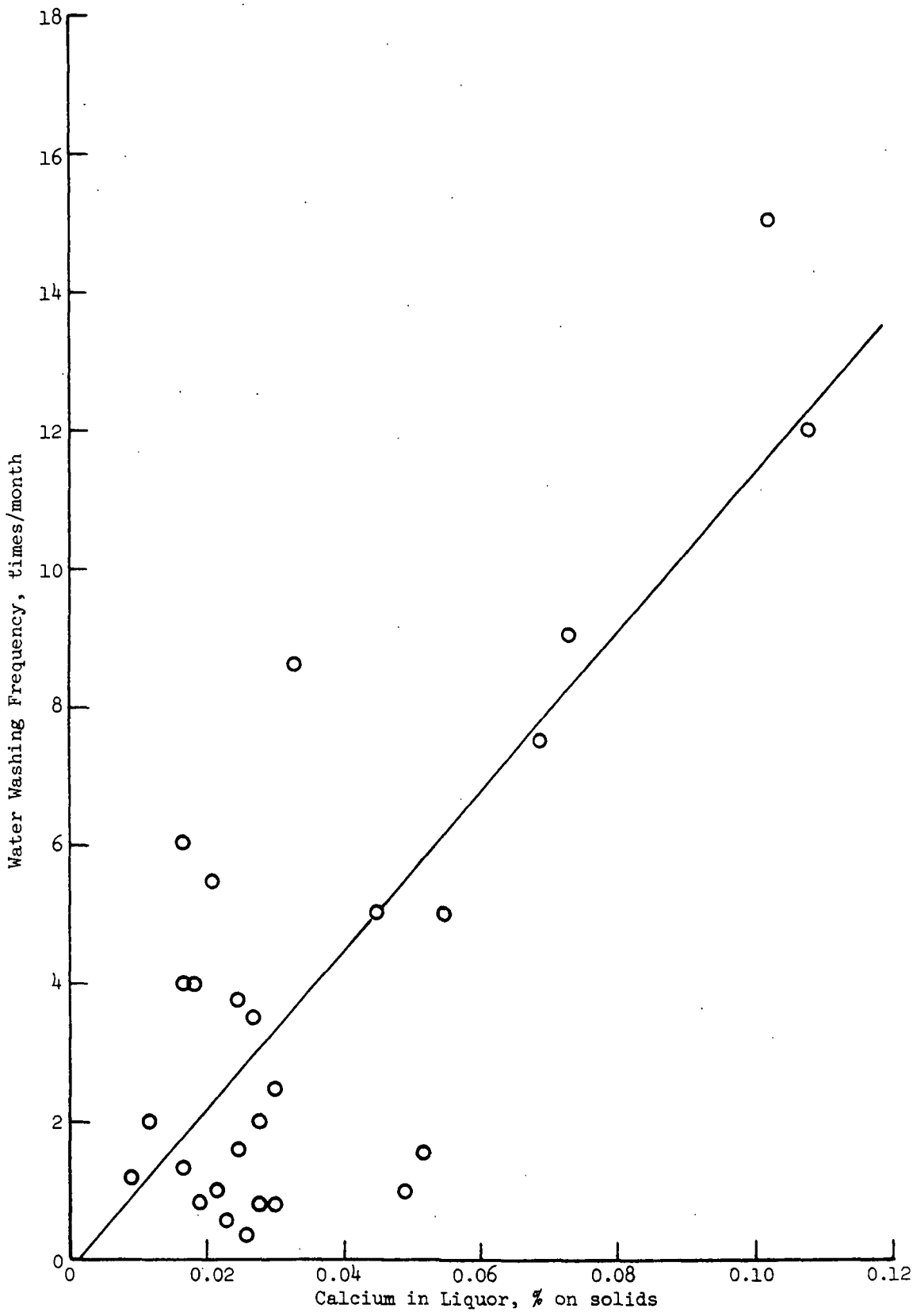

Figure 1. Scatter Diagram for Water Washing Frequency vs. Calcium in Liquor

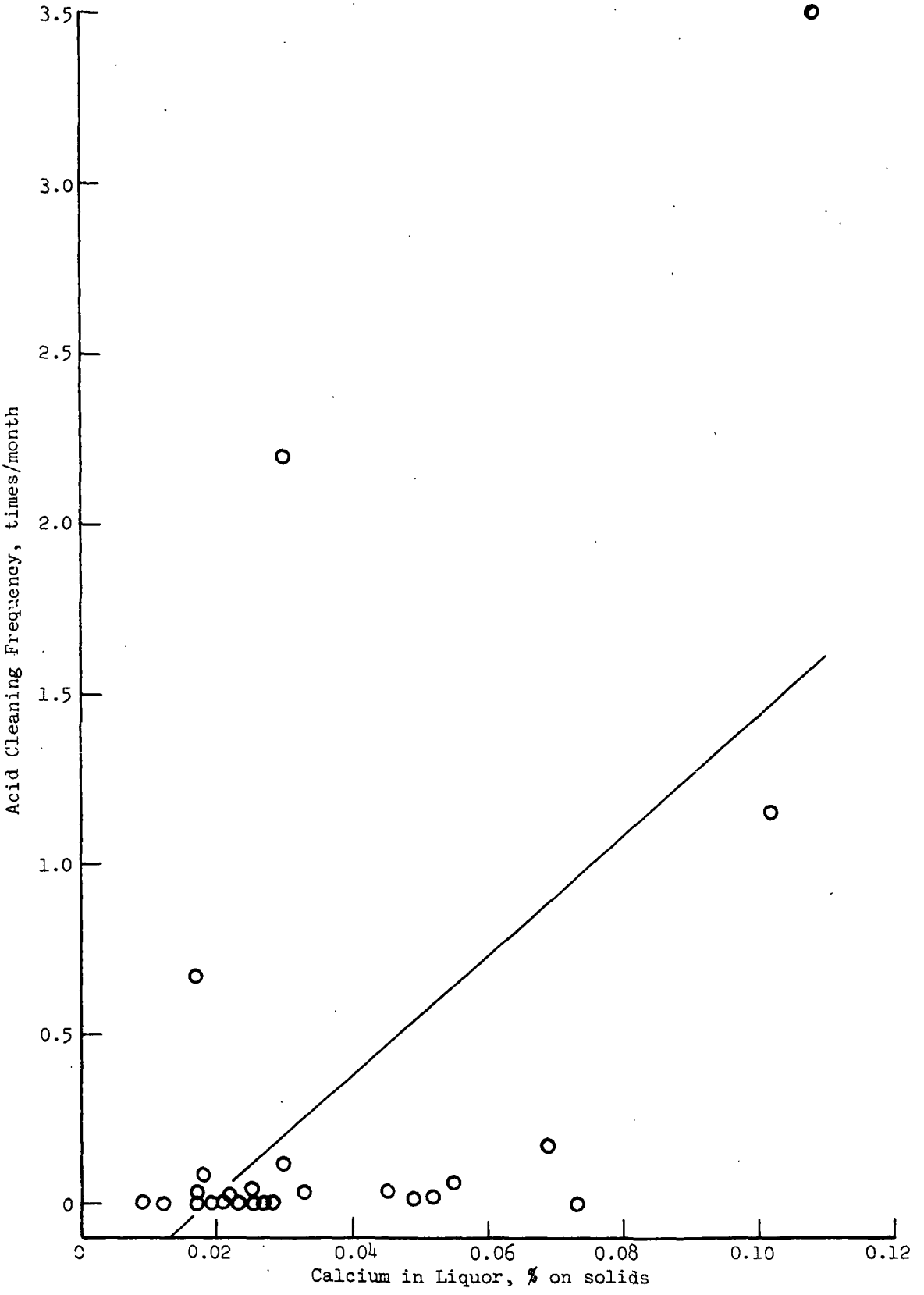

Figure 2. Scatter Diagram for Acid Cleaning Frequency vs. Calcium in Liquor

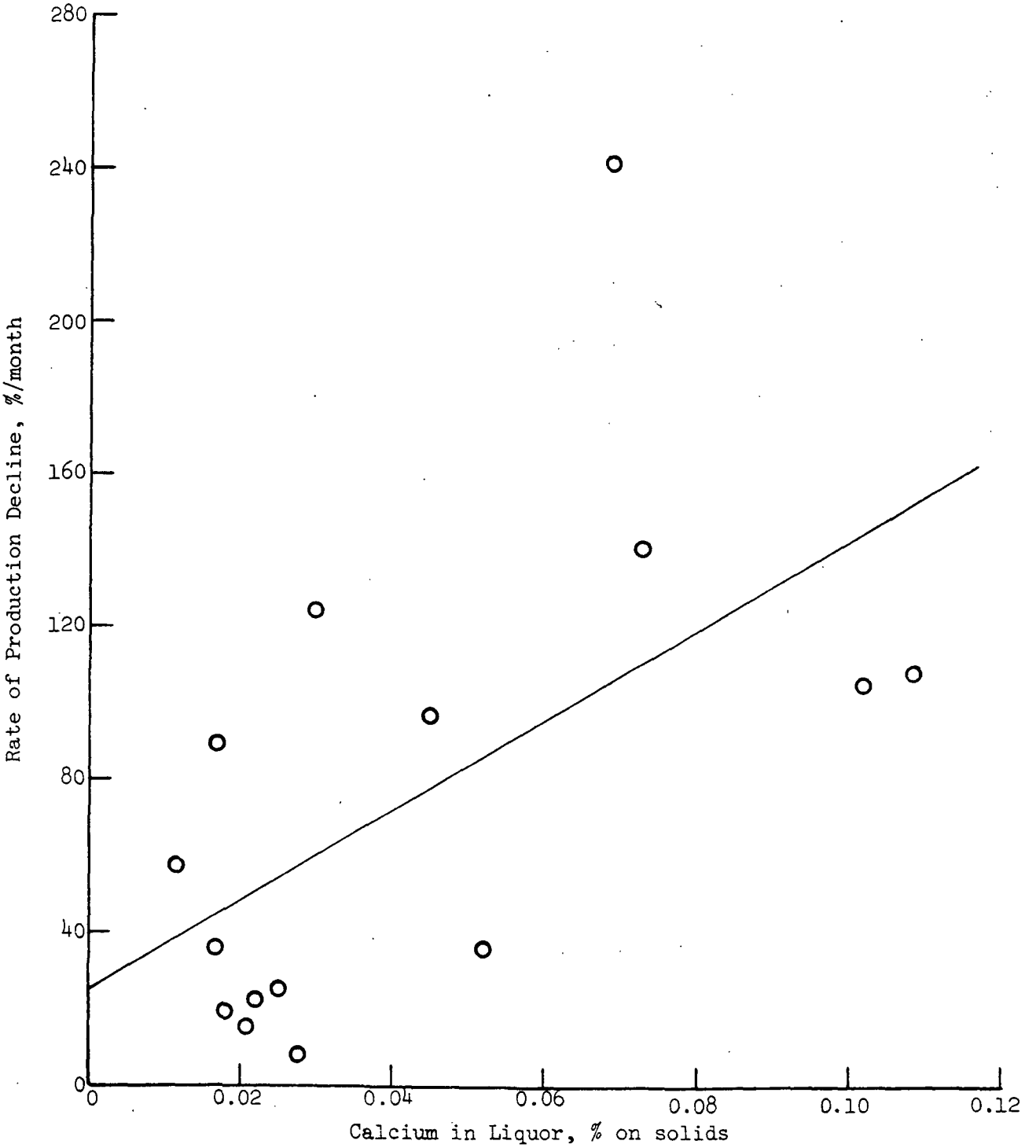

Figure 3. Scatter Diagram for Rate of Production Decline vs. Calcium in Liquor

reported no major scaling problem. The reasons for this are not known. There are also five mills (6, 7, 10, 11, and 17) lying substantially above the regression line. Three of these (6, 10, and 11) report carbonate-sulfate scale but do not report calcium scale. Mill 17 provides no information on scale composition, but states that they know of no scale problems. Only Mill 7 reports a calcium scale. It appears that water washing rates well above the regression line can be attributed either to soluble sulfate-carbonate scale or to the mill washing the evaporators as a routine maintenance procedure at intervals not necessarily related to evaporator performance. However, despite the many factors which can complicate the relationship, there is still a higher degree of correlation between water washing frequency and calcium in the liquor than between any other variable pair.

Figure 2 shows acid cleaning frequencies versus calcium in the liquor. Although the correlation coefficient is reasonably high (0.57), it is somewhat questionable whether or not a significant correlation exists. Only 6 mills out of 26 had acid cleaning frequencies greater than 0.1 per month. The correlation is actually dominated by the four mills with high acid cleaning frequencies. Of these, two have liquors which are quite high in calcium, and two have relatively low calcium levels.

Figure 3 shows a definite relationship between the rate of production decline and calcium content of the liquor although there is a good deal of scatter. This supports the concept that evaporator scaling problems increase as the calcium content of the liquor increases. Mills 3, 4, and 10 are significantly above the regression line. Mills 4 and 10 report some soluble scale, and this may be responsible for their relatively high performance loss. No explanation for the very high rate for Mill 3 is available. Mill 20 is again significantly

below the regression line. Another factor influencing this correlation is that only 15 mills provided sufficient data to permit the parameters to be calculated.

The fact that a significant correlation exists between the calcium content of the liquor and three different scaling indicators underscores the importance of calcium in the liquor to evaporator scaling. The most rational explanation for this is that calcium carbonate scale has the most pronounced effect on evaporator performance, and the rate of calcium carbonate scale deposition is governed by the calcium concentration in the liquor.

The fact that there is a significantly stronger correlation between calcium in the liquor and water washing frequencies than there is with acid cleaning frequencies is somewhat surprising. It is usually assumed that water washing will remove the soluble scales (e.g., Na_2CO_3 and Na_2SO_4), but not scales, such as $CaCO_3$, which are water insoluble. However, the data illustrated in Fig. 1 are strong evidence that boilouts with water do help control calcium scales. This could occur in a number of ways. Calcium carbonate could be deposited simultaneously with more soluble material. During the washing cycle, the soluble material would be dissolved leaving a residual $CaCO_3$ too weak to remain. Alternatively, thermal shocks during the boil-off period could act to remove water-insoluble material. In any event, these data clearly show that soluble scales cannot be distinguished from calcium scales solely by the relative frequencies of water washing and acid cleaning.

The only other liquor composition variable to correlate significantly with scaling parameters was the residual tall oil in the liquor. The correlation coefficients are relatively small in magnitude (0.43 and 0.41) and the slope of the regression line is negative (an increase in residual soap content correlated

with a decrease in water washing and acid cleaning frequencies). A scatter diagram for water washing frequency versus residual soap content is given in Fig. 4. Despite the variability there does appear to be a definite trend toward lower cleaning frequencies with higher residual soap levels. The correlation for acid cleaning frequency against residual soap is dominated by four mills (1, 2, 4, and 6). All four have low levels of residual soap. Two are hardwood kraft mills and would be expected to have low levels of extractives in the liquor. However, the other two use only about 20% hardwood.

If these correlations are truly significant, they suggest a beneficial effect of residual soap in the liquor, in apparent contradiction to a common view that maximum soap removal is needed to minimize scaling. That view arises from the fact that soaps will precipitate as liquor is concentrated and can form deposits on the tube walls. Soap-fiber combinations seem to be especially troublesome. However, a small amount of soap in the liquor might be helpful by tying up calcium. Several mills, which swing between hardwoods and softwoods, have reported that they experience evaporator scaling when processing hardwood liquor, which can then be removed while evaporating softwood liquor. There may be a connection between this experience and the weak correlation between scaling and residual soap found in this survey.

It is of interest to examine the effects of variables related to so-called soluble scales. A substantial number of mills reported soluble Na_2CO_3-Na_2SO_4 scales. These might be expected to be due to solubility limits of Na_2CO_3 and Na_2SO_4 being exceeded in the liquors. Solubility limits for Na_2CO_3 and Na_2SO_4 in black liquor were determined in an earlier project. These limits are summarized in Appendix III and expressed as critical solids content for each liquor in Table V. The degree of saturation that exists in the

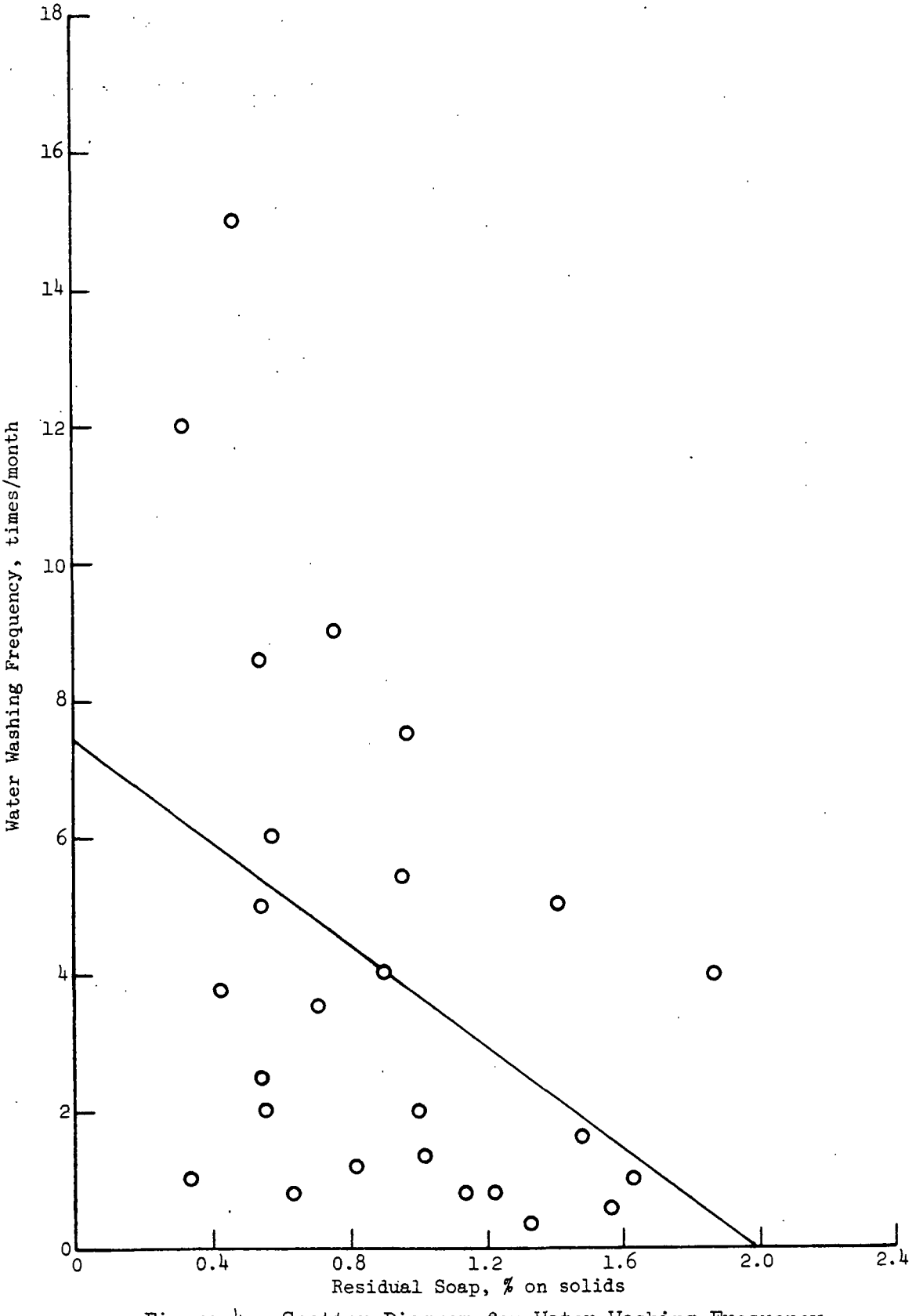

Figure 4. Scatter Diagram for Water Washing Frequency vs. Residual Soap in Liquor

evaporators is determined by the critical solids content of the liquor and the discharge solids content from the evaporator. It is calculated from

$$\text{Degree of saturation} = \frac{\text{discharge solids}/(100 - \text{discharge solids})}{\text{critical solids}/(100 - \text{critical solids})}$$

Values of the degree of saturation (in Na_2CO_3 and Na_2SO_4) leaving the evaporators are given in Table XV.

TABLE XV

DEGREE OF SATURATION AT EVAPORATOR DISCHARGE

Mill No.	Degree of Saturation	Mill No.	Degree of Saturation	Mill No.	Degree of Saturation	Mill No.	Degree of Saturation
1	0.566	9	0.845	17	0.761	25	0.75
2	0.928	10	0.875	18	0.588	26	0.709
3	0.865	11	1.37	19	1.037	27	0.828
4	0.806	12	0.812	20	0.985	28	1.045
5	0.608	13	0.842	21	0.883		
6	0.947	14	1.092	22	0.802	47	0.34
7	0.997	15	0.913	23	0.842		
8	0.845	16	0.723	24	0.873		

A summary of correlation coefficients for soluble scale parameters is given in Table XVI. Negative values of the correlation coefficient are used to designate correlations where the slope of the regression line is negative (an increase in one variable correlates with a decrease in the other).

The only variable combination showing any correlation is the rate of production decline versus residual active alkali. A scatter diagram for this variable pair is given in Fig. 5. The regression line indicates that there is

a reduction in scaling with increased residual alkali. This is in agreement with reported industry experience. However, there is a great deal of scatter in the data and the number of points are limited. Thus, the significance of the correlation is marginal. The amount of residual active alkali in the liquor is greater than 5% of the total solids in almost all cases. This would correspond to a concentration of about 8 g/liter as Na_2O in weak liquor at 15% solids.

TABLE XVI

CORRELATION COEFFICIENTS FOR SOLUBLE SCALE

Black Liquor Composition	Water Washing Frequency	Rate of Production Decline
Na_2CO_3	0.30	0.12
Na_2SO_4	-0.09	0.07
Residual active alkali	-0.18	-0.37
$Na_2CO_3 + Na_2SO_4$	0.14	0.13
Critical solids	-0.07	-0.04
Degree of saturation	-0.10	-0.29

None of the parameters related to the solubility of Na_2CO_3 and Na_2SO_4 in black liquor showed any significant correlation with scaling. This was a very surprising result of the survey. Possible explanations for this include:

1. Calcium scaling may dominate the scaling behavior to the extent that factors governing soluble scale formation are obliterated.
2. All liquors tend to approach saturation in Na_2CO_3 and Na_2SO_4 in the vicinity of 50% solids. The approach to supersaturation may then be controlled by local boiling conditions in the tube rather than bulk concentrations.

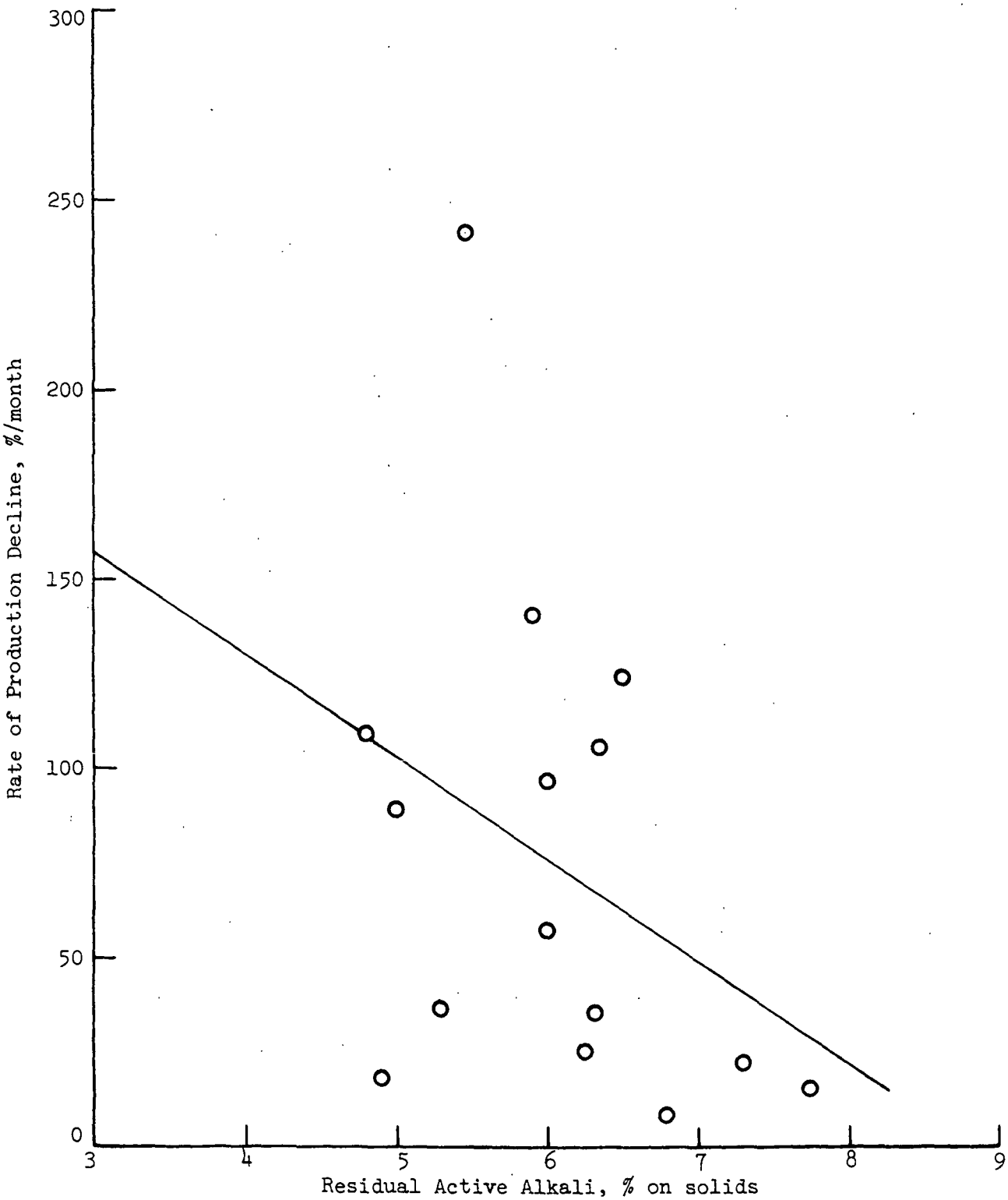

Figure 5. Scatter Diagram for Rate of Production Decline vs. Residual Active Alkali in Liquor

3. Soluble scale formation may be much more complex than a simple solubility phenomenon.

Correlation with Operating Variables

A summary of the correlation coefficients between the data on evaporator scaling in Table III and the operating data in Tables IV, VIII, IX, and X is given in Table XVII. Significant correlation coefficients are underlined. Spurious or chance correlations are indicated by parentheses.

TABLE XVII

CORRELATION OF SCALING EXPERIENCE WITH OPERATING VARIABLES

	Water Washing Frequency	Acid Cleaning Frequency	Mechanical Cleaning Frequency	Production Loss Between Cleanings	Rate of Production Decline
Discharge liquor solids content	0.11	0.29	0.11	0.07	0.25
Av. heat flux	0.05	0.16	0.02	0.21	0.42
Av. thermal driving force	0.59	0.16	0.04	0.36	0.18
Av. heat transfer coefficient	0.48	0.20	0.07	0.05	0.46
Steam saturation temp.	0.27	0.05	0.00	0.10	0.02
Production ratio	0.04	0.11	0.22	0.14	0.09
Amount of hardwood	0.26	0.37	0.17	0.10	0.39
Amount of whole tree chips	(0.42)	0.14	0.19	0.03	0.14
Storage time	0.02	0.01	0.26	0.04	0.09
Pulp yield	0.13	0.15	0.16	(0.38)	(0.39)
White liquor					
Active alkali	(0.40)	0.22	0.09	0.14	0.06
Na_2S	0.26	0.24	0.12	0.29	0.24
Na_2CO_3	0.20	0.16	0.01	0.17	0.29
Na_2SO_4	0.01	0.18	(0.57)	(0.48)	(0.54)
Calcium	0.03	0.11	0.12	0.03	0.11

Only five variable pairs show significant correlations, and these are relatively weak. The water washing frequency correlates with the average thermal driving force and average heat transfer coefficient, and the rate of production decline correlates with the average heat flux, the average heat transfer coefficient and the amount of hardwood used.

The strongest correlation (0.59) is between the water washing frequency and the average thermal driving force. A scatter diagram for this pair is given in Fig. 6. The regression line is also shown. Most of the data are clustered at the low end of the ΔT range, with relatively few points at higher ΔT's, but a correlation is definitely indicated. It does not appear likely that there is a cause and effect relationship between these two variables. Instead, both may be considered as responses to evaporator scaling. As scaling proceeds, the heat transfer capacity of the evaporator is reduced. One method of countering this reduction in capacity is to increase the ΔT over the evaporator. When it is no longer possible to maintain production by increasing the ΔT, it becomes necessary to clean the heat transfer surface. Thus, a correlation between this variable pair is not unexpected. The average ΔT is a strong function of the number of effects. The two mills (9 and 43) which are furthest below the regression line have only four effects. The selection of the number of effects can be due to factors entirely unrelated to scaling.

Definite correlations between the average heat transfer coefficient and the water washing frequency and the rate of production decline also exist. Scatter diagrams and regression lines for these pairs are given in Fig. 7 and 8, respectively. In both cases the average coefficient tends to increase as the scaling parameter decreases. These correlations can be interpreted as being reflections of the increased resistance to heat transfer caused by scale.

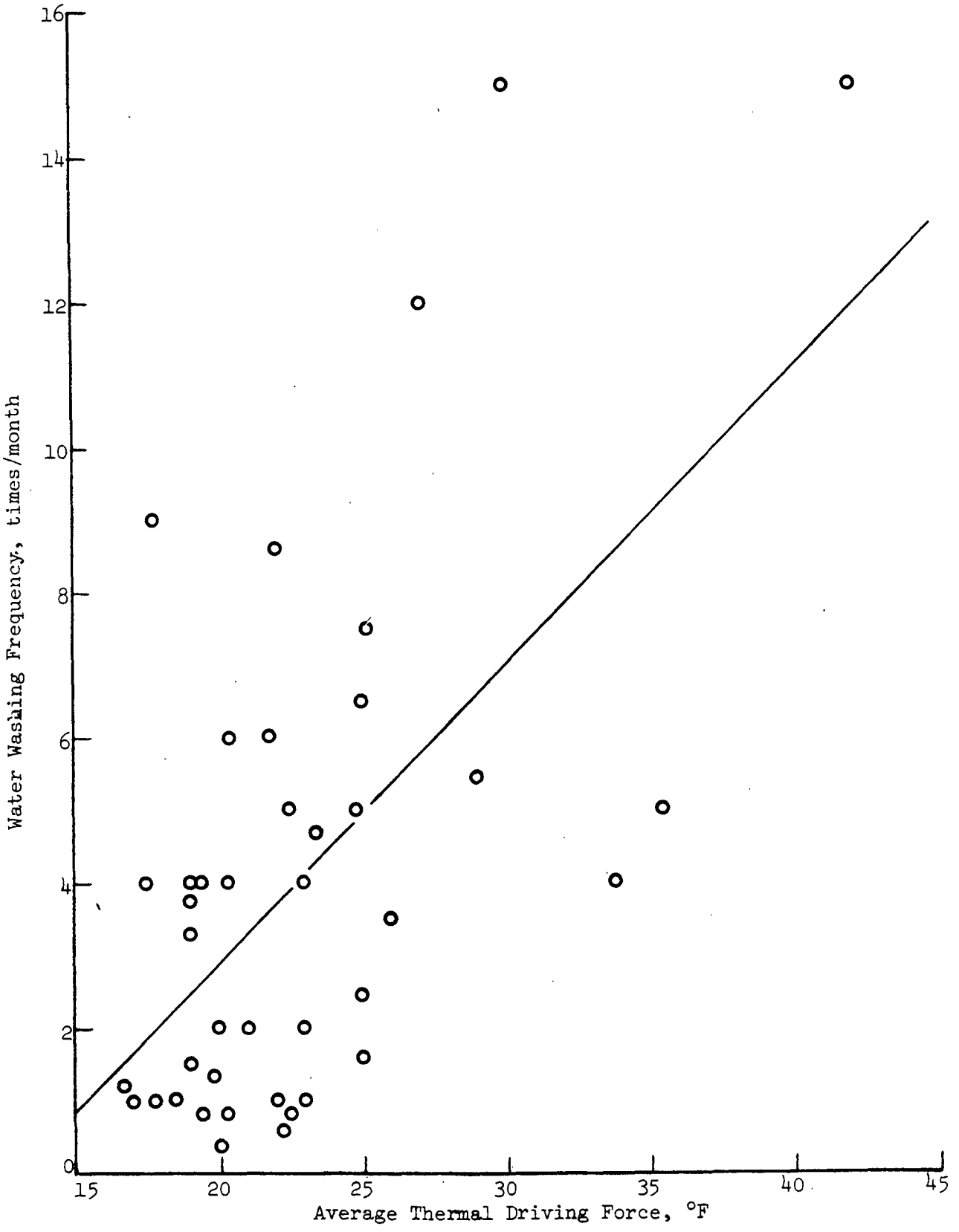

Figure 6. Scatter Diagram for Water Washing Frequency vs. Average Thermal Driving Force

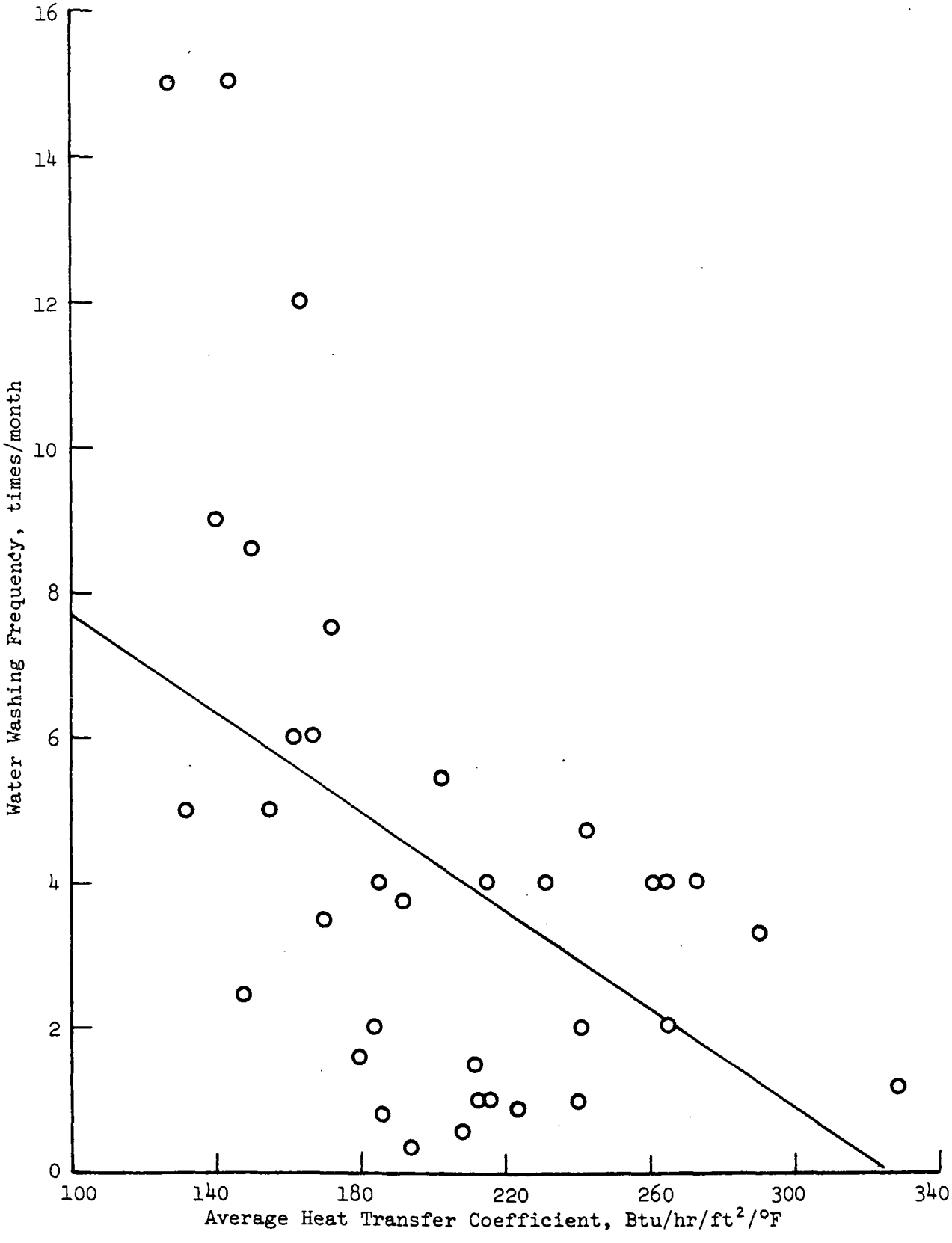

Figure 7. Scatter Diagram for Water Washing Frequency vs. Average Heat Transfer Coefficient

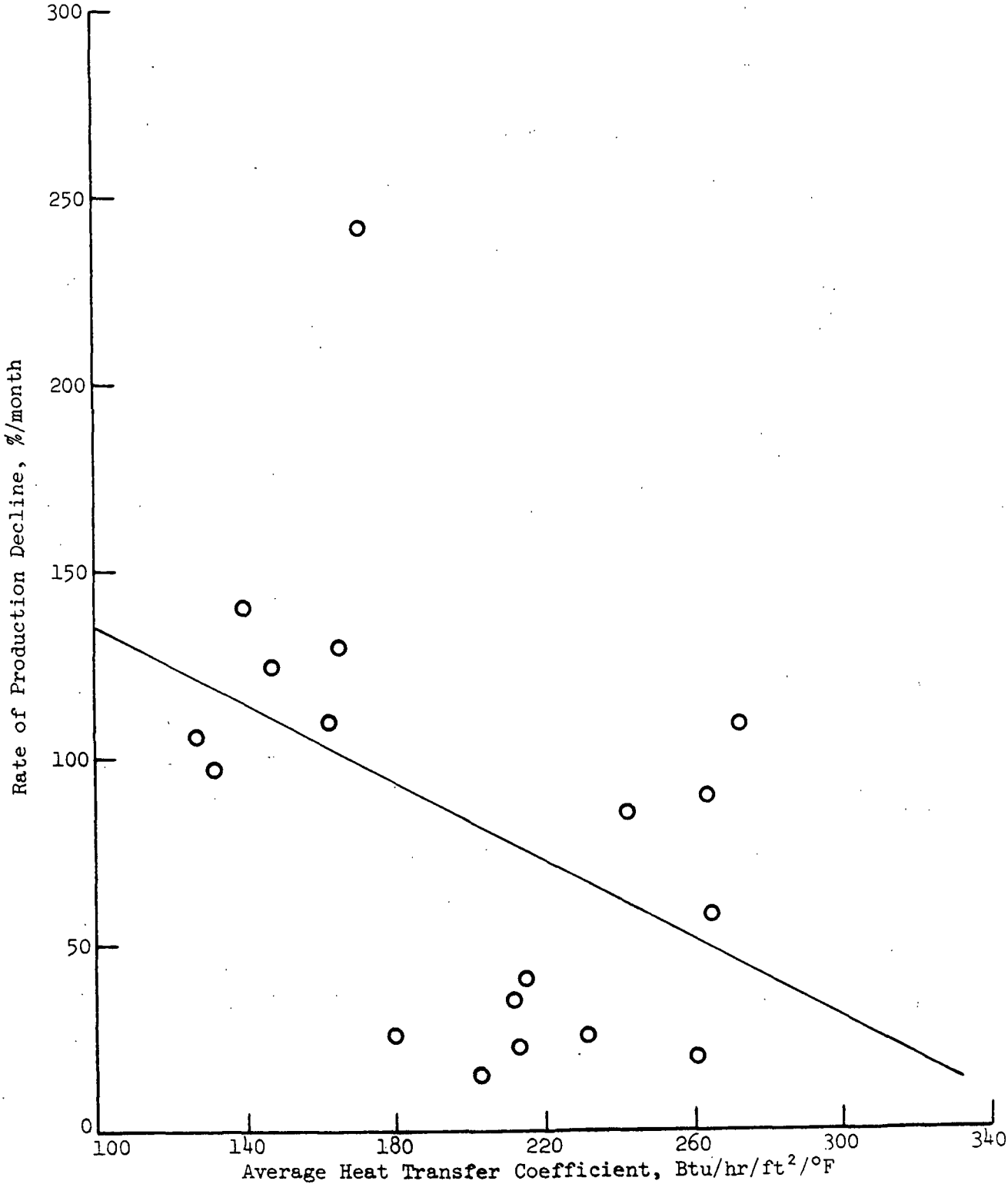

Figure 8. Scatter Diagram for Rate of Production Decline vs. Average Heat Transfer Coefficient

The weak correlation between the average heat flux and the rate of production decline (correlation coefficient of 0.42, scatter diagram not shown) is very similar and due to the same cause.

Finally, there is a weak correlation (correlation coefficient of 0.39) between the rate of production decline and the amount of hardwood used. A scatter diagram and the regression line for this pair of variables are shown in Fig. 9. This correlation is quite marginal. It is due almost entirely to the fact that all three of the mills using very high proportions of hardwood experienced high values for the rate of production decline.

All of the significant correlations with scaling parameters are summarized in Table XVIII. Negative values of the correlation coefficient are used to indicate those cases where the slope of the regression line is negative. The dominant role played by the calcium content of the liquor is clearly evident.

HEAT TRANSFER COEFFICIENTS

The survey data indicate a better than two-to-one range in values of the average heat transfer coefficients for the evaporator systems. This is somewhat surprising, since the average heat transfer coefficient is a measure of the productivity of an evaporator. A mill with an average coefficient twice as high as another has the capability of evaporating twice as much liquor with the same amount of evaporator surface. The correlation of average heat transfer coefficients with scaling parameters was discussed in the previous section. There is a definite tendency for lower average heat transfer coefficients with increased scaling. However, other factors than scaling may be involved in the wide range in heat transfer coefficients. It is of interest, therefore, to examine the effects of liquor composition, and evaporator design and operating variables on the heat transfer coefficient itself.

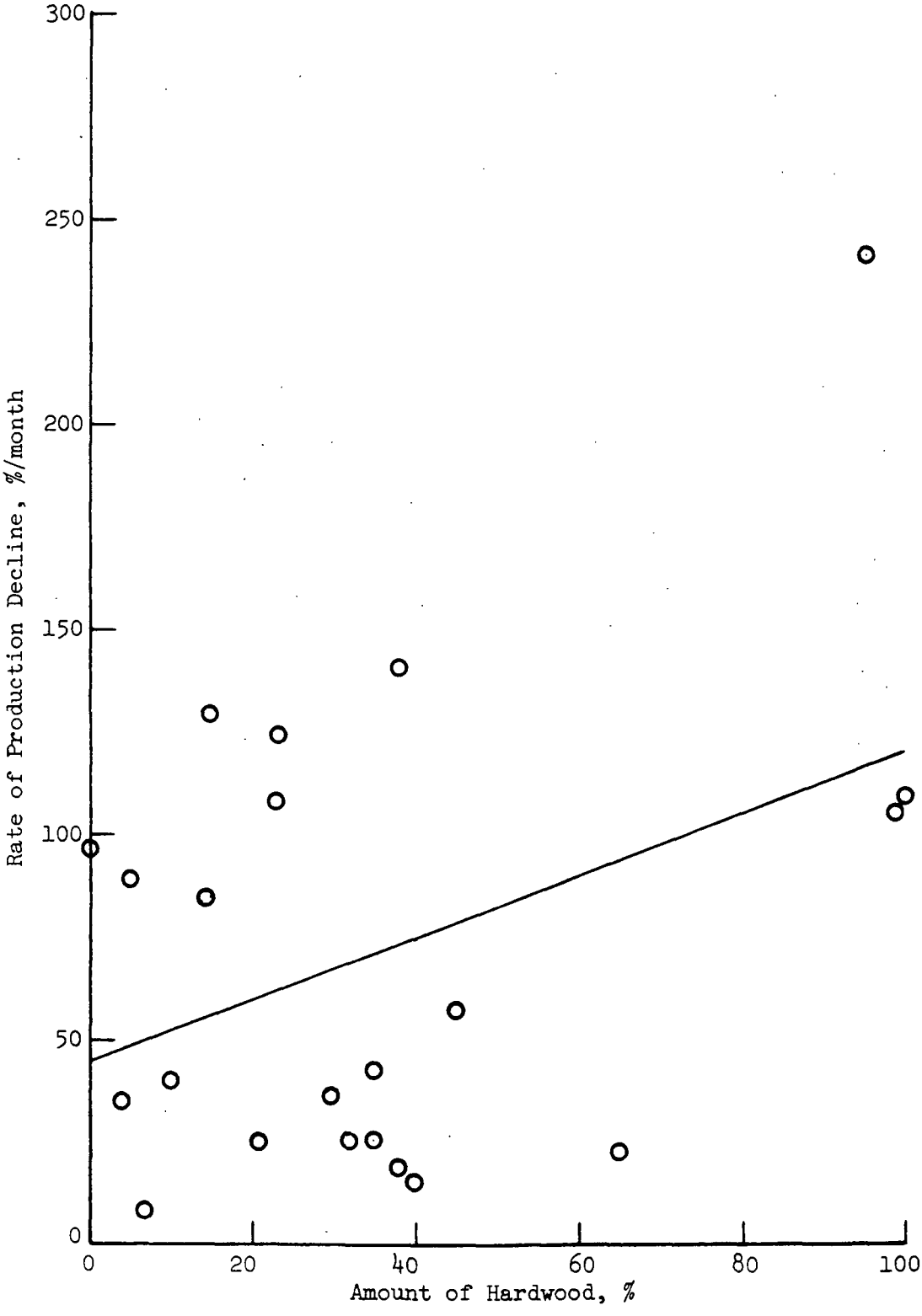

Figure 9. Scatter Diagram for Rate of Production Decline vs. Amount of Hardwood Used

TABLE XVIII

SUMMARY OF SIGNIFICANT CORRELATIONS FOR SCALING RATE DATA

Dependent Variable	Independent Variable	Correlation Coefficient
Water washing frequency	Calcium in liquor (emis. spec.)	0.80
Water washing frequency	Calcium in liquor (atom. abs.)	0.78
Acid cleaning frequency	Calcium in liquor (emis. spec.)	0.63
Rate of production decline	Calcium in liquor (atom. abs.)	0.58
Acid cleaning frequency	Calcium in liquor (atom. abs.)	0.57
Rate of production decline	Calcium in liquor (emis. spec.)	0.46
Water washing frequency	Residual soap in liquor	-0.43
Acid cleaning frequency	Residual soap in liquor	-0.41[a]
Water washing frequency	Average evaporator ΔT	0.59[b]
Water washing frequency	Average heat transfer coefficient	-0.48
Rate of production decline	Average heat transfer coefficient	-0.46
Rate of production decline	Average heat flux	-0.42
Rate of production decline	Amount of hardwood used	0.39[b]

[a] Controlled by 4 points out of 25.

[b] Strongly influenced by one point.

A summary of correlation coefficients between the average heat transfer coefficient and liquor composition and operating variables is given in Table XIX. The significant correlations are underlined and spurious correlations are indicated by parentheses. The variables which show significant correlations with the average heat transfer coefficient are calcium in the liquor, average heat flux, thermal driving force, saturated steam temperature and the number of effects.

TABLE XIX

CORRELATIONS WITH HEAT TRANSFER COEFFICIENTS

Liquor Composition Variables	Correlation Coefficient	Operational Variables	Correlation Coefficient
Sodium carbonate	0.03	Discharge liquor solids	0.20
Sodium sulfate	0.01	Heat flux	0.59
Residual active alkali	0.02	Thermal driving force	0.49
Total sodium	0.14	Saturated steam temp.	0.37
Calcium A.A.	0.53	Production ratio	(0.33)
Potassium	0.09		
Residual soap	0.24	Number of effects	0.29
Fiber	0.09	Tube length	0.15
Critical solids content	0.09		
		Amount of hardwood	0.07
Boron	(0.33)	Amount of whole tree chips	0.25
Silicon	0.24	Wood storage time	0.04
Manganese	0.14		
Iron	0.01	Pulp yield	0.07
Magnesium	0.22		
Aluminum	(0.32)		
Vanadium	0.02		
Calcium E.S.	0.52		
Copper	0.09		

The correlation with calcium in the liquor is another indication of the dominant role played by this parameter in evaporator scaling and evaporator performance. It is further evidence that calcium scaling is the single most significant factor in the operation of black liquor evaporators.

The correlation of the heat transfer coefficient with the heat flux and thermal driving force is primarily a reflection of the fact that the coefficient is calculated from these two quantities.

$$\text{Average Heat Transfer Coefficient} = \frac{\text{Heat Flux}}{\text{Thermal Driving Force}}$$

Any functional effect of these variables aside from the definition is obscured by the direct calculated relationship.

The correlation of the heat transfer coefficient with the saturated steam temperature is weak but distinct. The slope of the regression line is negative so that an increase in steam temperature is associated with a decreasing coefficient. It is likely that the decreased heat transfer coefficient is the cause and the higher steam temperature the effect. Increasing the steam temperature is one way to maintain evaporator capacity in the face of declining heat transfer coefficients, since it increases the thermal driving force.

The weak correlation with the number of effects appears to be similar. Reducing the number of effects is another way of maintaining evaporator capacity despite low heat transfer coefficients, since it also increases the thermal driving force.

The apparent correlation between the heat transfer coefficient and the production ratio appears to be spurious. A scatter diagram for this pair of variables is given in Fig. 10. No definite trend is evident in these data. It should be noted that the bulk of the mills which reported are operating below the design capacity of the evaporators. This could be due to a number of factors not related to scaling.

LIQUOR COMPOSITION

A summary of correlation coefficients between liquor composition and operating variables is given in Table XX. Significant correlations are underlined and spurious correlations indicated by parentheses. The combinations yielding significant correlations include calcium and potassium content of the liquor versus amount of hardwoods, Na_2SO_4 and critical solids in black liquor versus Na_2SO_4 in white liquor, aluminum in black liquor versus pulp yield, and residual active alkali and total sodium versus discharge liquor solids content.

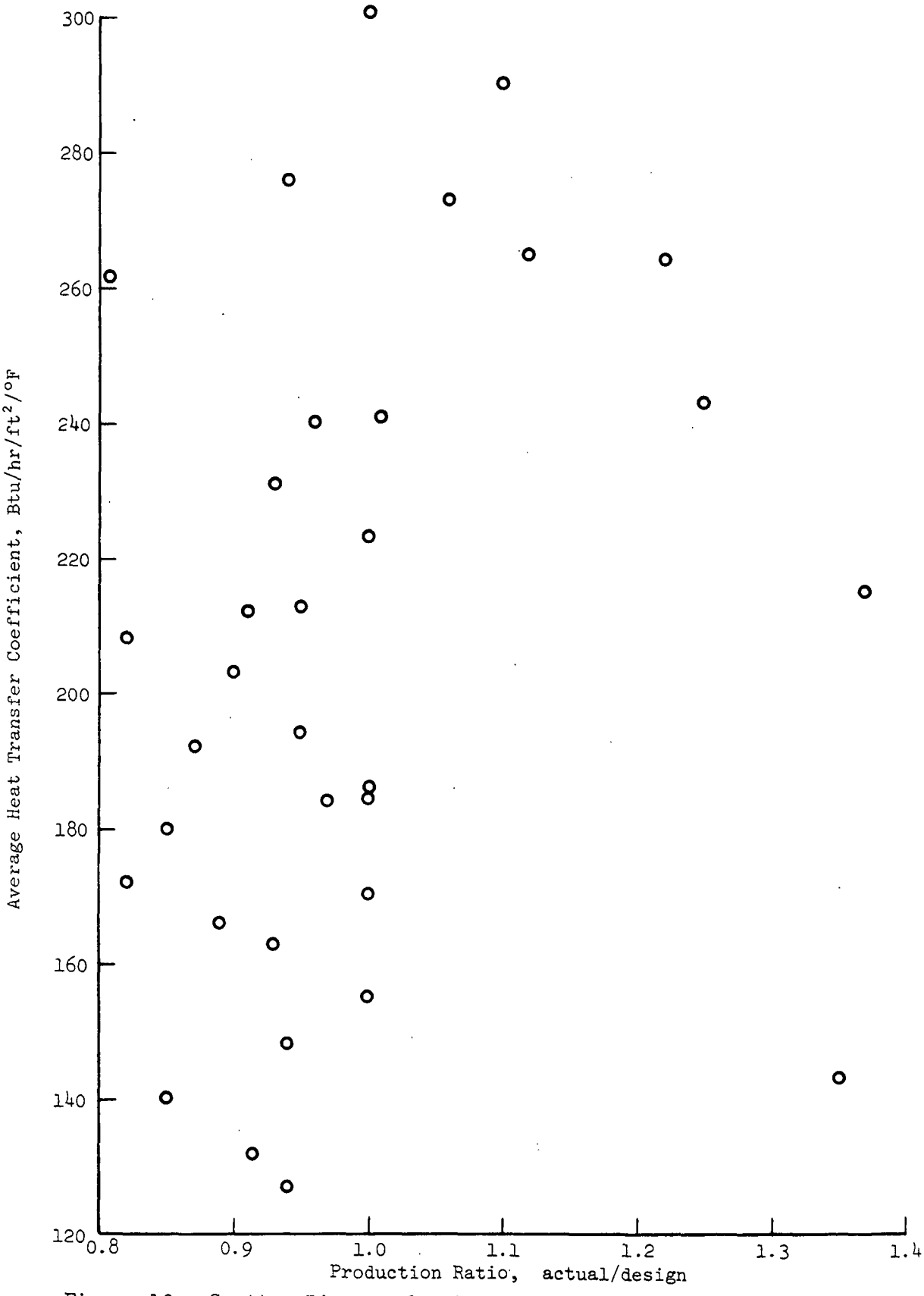

Figure 10. Scatter Diagram for Average Heat Transfer Coefficient vs. the Ratio of the Actual Evaporation Rate to the Design Value

TABLE XX

CORRELATION COEFFICIENTS FOR LIQUOR COMPOSITION VS. OPERATING VARIABLES

	Discharge Liquor Solids	Amount of Hardwood	Amount of Whole Tree Chips	Wood Storage Time	Pulp Yield	White Liquor				
						Active Alkali	Na_2S	Na_2CO_3	Na_2SO_4	Calcium
Sodium carbonate	0.18	0.28	0.07	0.06	0.02	0.22	0.08	0.20	0.11	0.19
Sodium sulfate	0.07	0.13	0.10	0.06	0.10	(0.37)	0.12	0.06	0.70	0.27
Residual active alkali	0.35	0.18	0.12	0.08	0.30	0.08	0.14	0.10	0.04	0.08
Total sodium	0.47	0.06	0.12	0.12	0.26	0.15	0.10	0.05	0.29	0.11
Calcium A.A.	0.31	0.57	0.12	0.17	0.08	(0.44)	(0.54)	(0.60)	0.05	0.01
Potassium	(0.36)	0.56	0.04	0.22	(0.43)	0.13	0.04	0.15	0.03	0.02
Residual soap	0.25	0.27	0.12	0.06	0.22	0.30	0.01	0.20	0.08	(0.44)
Fiber	0.29	0.15	0.25	0.01	0.20	0.07	0.08	0.01	0.10	0.20
Critical solids	(0.33)	0.12	0.08	0.11	0.15	0.01	0.15	0.05	0.58	0.05
Boron	0.13	0.17	0.10	0.09	0.14	0.10	0.23	0.19	0.27	(0.65)
Silicon	0.19	0.04	0.08	0.00	0.24	0.12	0.04	0.25	0.14	0.19
Manganese	(0.35)	0.32	0.03	0.15	0.15	0.08	0.03	0.18	(0.33)	0.04
Iron	0.12	0.09	(0.39)	0.02	0.29	0.21	0.29	0.38	0.15	0.20
Magnesium	0.03	0.25	(0.38)	0.21	0.13	0.19	0.21	0.21	0.06	0.12
Aluminum	0.02	0.23	0.16	0.09	0.62	0.12	0.09	0.01	0.08	0.09
Vanadium	0.05	0.00	0.15	0.03	0.02	0.19	0.19	0.23	0.15	(0.31)
Calcium E.S.	0.25	0.63	0.05	0.13	0.19	(0.49)	(0.45)	(0.51)	0.09	0.15
Copper	0.10	0.34	0.11	0.06	(0.54)	(0.57)	0.25	0.14	0.22	0.00

The correlation of calcium content of the liquors with the amount of hardwood used is relevant to the question of the origin of calcium in black liquor. A scatter diagram, including the regression line, for calcium content determined by atomic absorption and amount of hardwood is shown in Fig. 11. There is a great deal of variability, but a definite trend toward higher calcium levels with increased hardwood usage is evident. This may be contrasted with the lack of correlation (correlation coefficients of 0.01 and 0.15) between calcium in black liquor and reported values for calcium in white liquor. (These latter correlations involve only 15 mills, and this may have a bearing on the lack of correlation.) Similarly, no significant correlations were found (correlation coefficients of 0.08 and 0.15) between calcium in the black liquor and reported values for calcium in the mill water supply. These results would seem to indicate that the wood supply is the major source of calcium in the black liquor.

The correlation between Na_2SO_4 in black liquor and Na_2SO_4 in white liquor is quite significant. (The correlation of critical solids with Na_2SO_4 in white liquor is due to the relationship between critical solids and Na_2SO_4 in black liquor.) It is of interest that Na_2SO_4 is the only black liquor component to correlate with the concentration of that substance in the white liquor. It is somewhat surprising that a similar correlation did not hold for Na_2CO_3. This appears to indicate that the Na_2CO_3 content of black liquor is strongly affected by pulping reactions while the sulfate content is not. These results support the concept that the sulfate content of black liquor is governed by the reduction efficiency obtained in the recovery furnace.

A reasonably strong (correlation coefficient of 0.62) correlation between the aluminum content of black liquor and pulp yield is indicated. This is somewhat puzzling since there is no obvious reason why these two variables should be

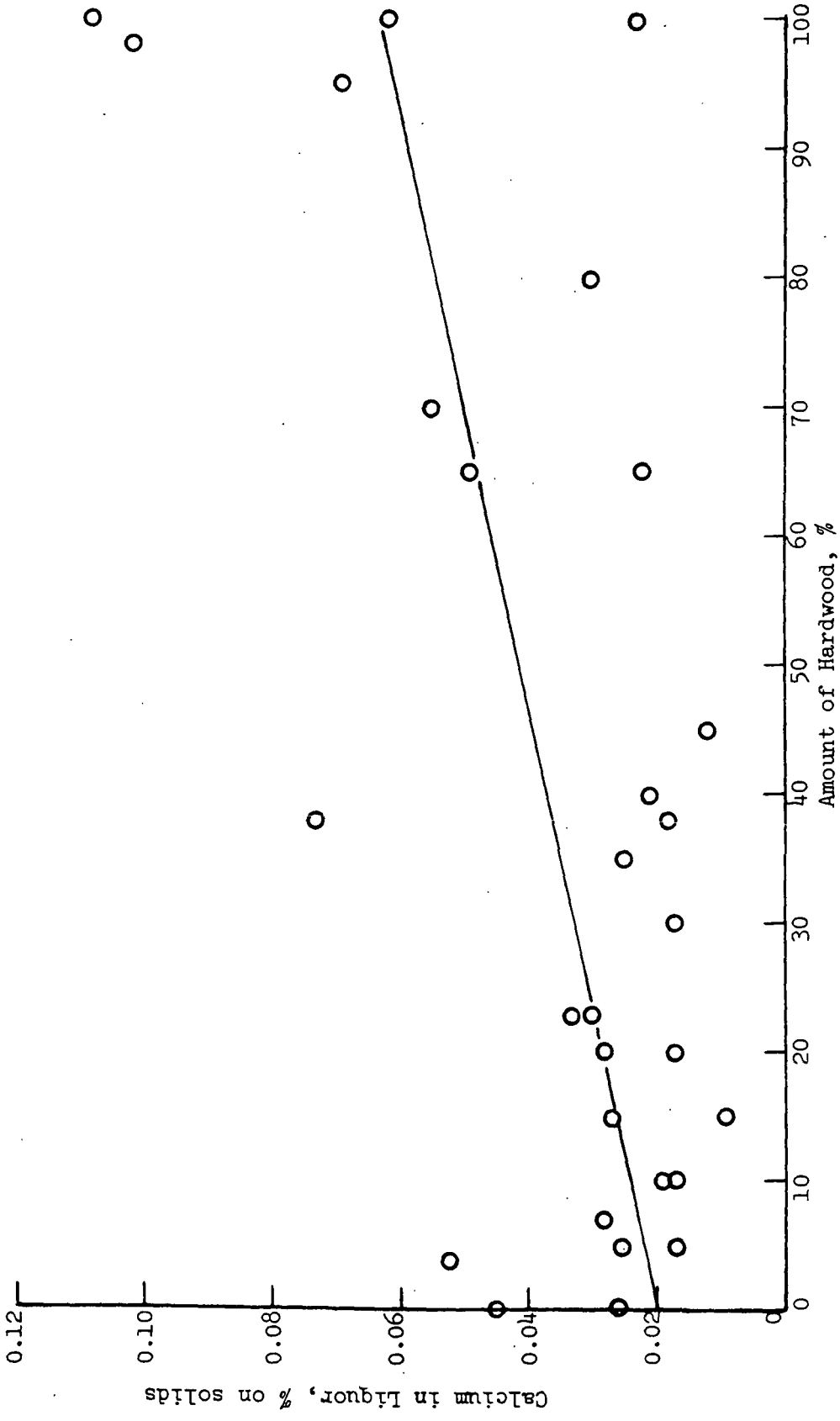

Figure 11. Scatter Diagram for Calcium in Liquor vs. the Amount of Hardwood Used

related. A scatter diagram for this variable pair is shown in Fig. 12. The correlation appears real. There is a definite tendency for higher aluminum levels at higher pulp yields. It does not appear that this correlation is due to the generally higher inorganic content of liquors from high yield pulps, since none of the other trace materials showed such a correlation. No explanation of this relationship is presently available.

Very weak correlations exist between the residual active alkali and total sodium contents of the liquor and the evaporator discharge solids content. In both cases, an increase in concentration of the black liquor component is associated with higher discharge solids. This is in agreement with the reported beneficial effect of residual active alkali. It is not clear why higher sodium contents should allow higher solids contents to be reached. If sodium is taken as a measure of the inorganic content of the liquor, this suggests that liquors containing more inorganic substances are easier to concentrate.

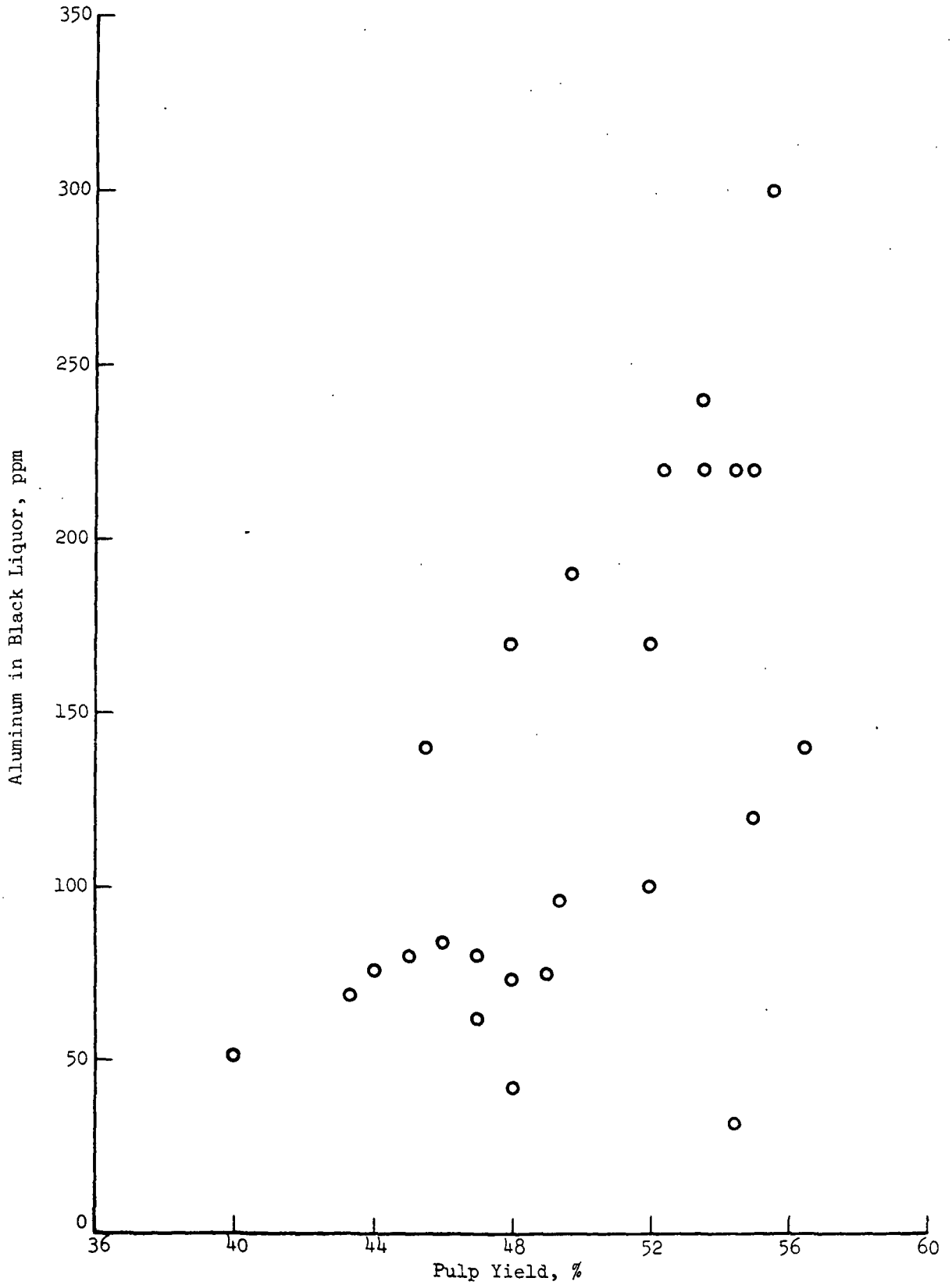

Figure 12. Scatter Diagram for Aluminum in Black Liquor vs. Pulp Yield

CONCLUSIONS

The most common scales are calcium scales (especially $CaCO_3$) and soluble scales (mainly Na_2CO_3 and Na_2SO_4). Other types of scales reported include silica, aluminum silicate, soap and fiber deposits, and ligneous material. Many mills experienced more than one kind of scale. The overall scaling behavior is then determined by the relative growth rates and ease of removal of these different types of scale.

Calcium scales appear to constitute a more serious problem in the industry than the so-called soluble scales. This is not due solely to the fact that calcium scales are more difficult to remove. Calcium scales can also play a dominant role in short-term evaporator productivity. The data obtained in this survey do not support the concept that rapid growing but easily removal soluble scales are responsible for most of the short-term degradation in performance while slow growing, insoluble calcium scales cause only a gradual deterioration in performance level. Instead they suggest that rapid growing calcium scales are very important.

There is a strong correlation between the water washing frequency and the calcium content of the liquors being evaporated. On the other hand, there are no significant correlations between water washing frequency and any parameters related to soluble scale formation. This is strong evidence that substantial amounts of calcium scales can be removed by boiling out the evaporator. The reason for this is unknown. It could be due to thermal shock to the deposits, removal of more soluble material from the scale matrix, or other reasons.

The most significant parameter affecting evaporator scaling is the calcium content of the liquor. There is no doubt that calcium in the black liquor

should be minimized. High calcium concentrations correlate strongly with increased scaling. There are indications that the amount of calcium in the liquor is influenced more by wood supply than by internal process conditions. A weak correlation was found between the calcium content of the liquor and the amount of hardwood processed. In contrast, no correlation was found between calcium in the black liquor and reported calcium in white liquor or in the mill water. The role of the wood supply as a potential source of calcium must be considered in developing methods for controlling liquor calcium content. Good white liquor clarity would help to minimize calcium in the white liquor (and, hence, presumably in the black liquor). However, white liquor does not seem to be the main source of calcium in black liquor. Thus, while good white liquor clarity would be useful in minimizing one source of calcium, it alone is probably insufficient to control calcium scaling.

A surprising result of the survey was the inability to find any significant correlation between scaling behavior and Na_2CO_3-Na_2SO_4 solubility limits in the liquor. None of the parameters known to be associated with carbonate-sulfate solubility showed any significant correlation with any of the parameters characterizing scaling. Part of the reason for this is undoubtedly the dominance of calcium scales. However, this may not be the whole answer. It is possible that soluble scale formation is not controlled by the bulk solubility of Na_2CO_3 and Na_2SO_4. Either local conditions along the tube wall could control the approach to saturation, or the net rate of scale formation could be governed by processes occurring at the liquor-scale interface.

It has been reported that maintaining high reduction and causticizing efficiencies (which would help to minimize levels of Na_2SO_4 and Na_2CO_3 in the liquor) helps to reduce scaling. The data obtained in this survey showed no

correlation between scaling and levels of these materials in either black or white liquor. Thus, the effectiveness of these measures to control scaling is not supported by the survey.

A correlation was found between residual soap in the liquor and scaling behavior. It was in the direction of a decrease in scaling with an increase in residual soap. This is in direct contradiction to the usual view that maximum soap removal leads to reduced scaling. These data indicate that some soap is beneficial, and that there may be an optimum degree of removal. This effect may be related to the ability of soap to tie up calcium.

A very weak correlation was established between the scaling rate and the amount of residual active alkali in the liquor. The tendency was toward a slight decline in the severity of scaling as residual active alkali increased. This is in agreement with reports that increased residual alkali is beneficial for scale prevention. The weakness of the correlation may be a reflection of the fact that most mills maintain residual alkali levels above the minimum needed. Eighty percent of the mills submitting liquor samples had levels of residual active alkali greater than 5% on the solids. This would correspond to 8 g/liter as Na_2O in weak liquor at 15% solids.

No correlation could be established between the measured fiber content of the liquor and scaling. This could be due in part to sampling problems and variability in fiber content of liquor in any given mill. Many mills reported fiber in their deposits.

Scaling appears to be the primary factor responsible for the variability in the average heat transfer coefficients for the evaporator systems. No other correlations were strong enough to indicate a controlling influence on evaporator performance.

ACKNOWLEDGMENTS

The author gratefully acknowledges the contributions of D. Sachs and H. Grady, who analyzed the liquor samples, B. D. Andrews, who helped assemble the data, and J. Bachhuber and J. Church, who assisted with the correlation analysis.

THE INSTITUTE OF PAPER CHEMISTRY

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APPENDIX I

SAMPLE QUESTIONNAIRE

Mill Identification: Company _____

Location _____

Person Completing Questionnaire: Name _____

Position _____

I. Definition of Process Conditions

A. Wood Supply

1. species (estimate proportions if possible)

pine _____%

mixed hardwoods _____%

Douglas fir _____%

other _____%, identify

2. geographical location of wood supply

__ southeast __ northeast __ northwest

__ midsouth __ north central __ other, specify

3. nature of wood supply, give proportions

roundwood _____% whole tree chips _____%

purchased chips _____% sawdust _____%

other _____%, specify

4. wood storage

storage time _____ months

method of storage:

5. barking

degree of bark removal: __ good __ fair __ poor

type of barking system:

6. dirt content

__ high __ average __ low

7. additional comments

B. Pulping Conditions

1. type of pulping process

kraft ____ TPD, NSSC _____ TPD, other--specify ____ TPD

if swinging between species give relative production rates:

2. bleached production ____ TPD

3. yield (if more than one process is involved give yields separately)

4. type of digesters

__ batch, production rate ___ TPD

__ continuous, production rate ____ TPD

5. amount of recirculating black liquor
% by volume of total ____

6. white liquor charge

effective alkali on o.d. wood _____%

7. white liquor analysis

active alkali (as Na_2O)	_____ g/l	or	____ lb/ft^3
sodium sulfide (as Na_2S)	_____ g/l	or	____ lb/ft^3
sodium carbonate (as Na_2CO_3)	_____ g/l	or	____ lb/ft^3
Sodium sulfate (as Na_2SO_4)	_____ g/l	or	____ lb/ft^3
calcium (as Ca)	_____ g/l	or	____ lb/ft^3

8. additional comments

C. Liquor Processing

1. characteristics of input water

source of pulp wash water:

source of water to causticizing plant:

mill water analysis:

Ca	____ ppm	Fe	____ ppm
Mg	____ ppm	Silica	____ ppm
R_2O_3	____ ppm	Cl^-	____ ppm
SO_4	____ ppm	Other	____ ppm

2. black liquor oxidation

__ weak __ strong __ none

Oxidation efficiency ____%

3. if pulping separate species, are liquor handled separately or blended

__ separately __ not applicable

__ blended comments:

4. soap removal

soap removal efficiency ____%

location in system

5. fiber content of liquor ___g/l or ____ lb/gal

is a filter used? ___ yes ___ no

6. extraneous material added to liquor (what added, where)

7. are additives used for scale control? (what kind, dosage)

8. describe any unusual processing steps

II. Evaporator Description and Performance

A. Description of system

1. number and arrangement of evaporators (number of effects, number of bodies, liquor flow sequence, use of concentrators, (attach flow sheet, if available)

2. type of evaporators (manufacturers, straight or modified LTV's, other types, internal preheat, number of passes, etc.)

3. geometry:

	conventional effects	concentrators
number of tubes per effect	_____	_____
tube diameter, inches	_____	_____
tube length, feet	_____	_____

4. liquor solids content

solids entering evaporators	____%
solids entering 1st effect	____%
solids leaving 1st effect	____%
solids entering concentrator	____%
solids leaving concentrator	____%

B. Performance

1. production rates

average rate: lb/hr evaporated ____ overall ΔT ____ °F

design rate: lb/hr evaporated ____ overall ΔT ____ °F

2. loss of capacity between washes

	lb. evap./hr.	overall ΔT, °F
just before cleaning:	_____	_____
just after cleaning:	_____	_____

3. cleaning frequencies

frequency of water washing: _____

frequency of acid cleaning: _____

frequency of mechanical cleaning: _____

comments:

C. Scaling Conditions

1. location of scale (effects which scale, location within effect, if known)

2. conditions in scale forming area

liquor solids range _____

liquor temperature, °F _____

steam temperature, °F _____

liquor velocity _____

3. tube wall conditions in scaling zone

tube material: _____

age of tubes: _____

number of times acid cleaned: _____

number of times mechanically cleaned: _____

comments:

III. Liquor and Scale Composition

A. Scale Composition

1. general types of scale encountered

__ carbonate-sulfate scale __ silica scale

__ calcium scale __ other

comments:

2. available analyses of scales or deposits

3. if actual samples of scale are available we would appreciate obtaining some for our own analysis (see address below)

B. Liquor Composition

1. any available data on black liquor composition especially on residual active alkali, carbonate and sulfidity

2. please send a sample of black liquor

(approximately one quart taken from effect just ahead of the ones which scale, fill to avoid oxidation in transport, store in cold place before sending, identify the liquor)

Please send liquor and scale samples to:

The Institute of Paper Chemistry
Attention: Dr. T. M. Grace
1043 East South River Street
Appleton, Wisconsin 54911

APPENDIX II

ANALYSIS OF LIQUOR SAMPLES

The following procedures were used in the analyses of the liquor samples.

Liquor solids: Determined in accordance with TAPPI Procedure T 650 su-71. This involves oven drying at 105°C and the use of an inert surface extender.

Na_2CO_3: Determined by a procedure described in T 624 os-68. A weighed liquor sample is treated with acid and the CO_2 released is measured by absorbing it on ascarite.

Na_2SO_4: Determined by a procedure described in T 625 ts-63. Sulfate is determined by precipitation as $BaSO_4$. The liquor is first treated with acid and filtered to destroy carbonate and remove lignin.

Residual active alkali: Determined by titration of a liquor sample with HCl down to pH 8.3 followed by a correction for the Na_2CO_3 present (from CO_2 evolution).

Total sodium: Determined by flame ionization spectrophotometry after digestion of the sample with perchoric acid as described in T 625 ts-63.

Calcium: Determined by atomic absorption spectroscopy on perchloric acid digested samples. Lanthanum was added to suppress sodium interference.

Potassium: Determined by atomic absorption spectroscopy. It can also be estimated from the difference between a sulfated ash determination and the amount of sulfated ash expected from the measured total sodium.

Residual soap: Determined by extraction with petroleum ether. The procedure was taken from a paper "Estimation of Tall Oil in Sulfate Black Liquor" by Saltsman and Kuiken, Tappi 42:11(Nov., 1959).

Fiber: Determined as the weight retained on filtering liquors through fritted glass crucibles of coarse porosity.

Trace metals: Determined by flame emission spectroscopy.

APPENDIX III

DETERMINATION OF Na_2CO_3-Na_2SO_4 SATURATION

Solubility limits for Na_2CO_3 and Na_2SO_4 in black liquor were determined in a previous study. The results obtained are summarized in Fig. 13 and 14. The main parameters governing the solubility are the combined Na_2CO_3 and Na_2SO_4 concentrations and the effective sodium content of the liquor. The effective sodium content is defined as follows:

$$\text{Effective sodium} = \text{Total sodium} - 23\left(\frac{Na_2CO_3}{53} + \frac{Na_2SO_4}{71}\right).$$

The basic solubility relationship is presented in Fig. 13. A correction factor, to account for the small effects due to relative proportions of Na_2CO_3 and Na_2SO_4, is given in Fig. 14.

The critical solids content of a liquor (the solids level at which it just becomes saturated with respect to Na_2CO_3 and Na_2SO_4) is a unique parameter for any given liquor. It is determined by the Na_2CO_3, Na_2SO_4, and total Na content of the liquor. The procedure for calculating the critical solids content is as follows:

1. From the measured Na_2CO_3, Na_2SO_4, and total Na contents of the liquor, calculate Na_2CO_3+Na_2SO_4 and effective sodium.
2. Go to Fig. 13 and read off the corresponding liquor solids content, S.
3. Using S, the effective sodium content and the Na_2CO_3/Na_2SO_4 ratio, go to Fig. 14 and determine the correction factor, f.
4. Calculate the corrected critical solids according to critical solids $= \frac{fS}{1-(1-f)S}$.

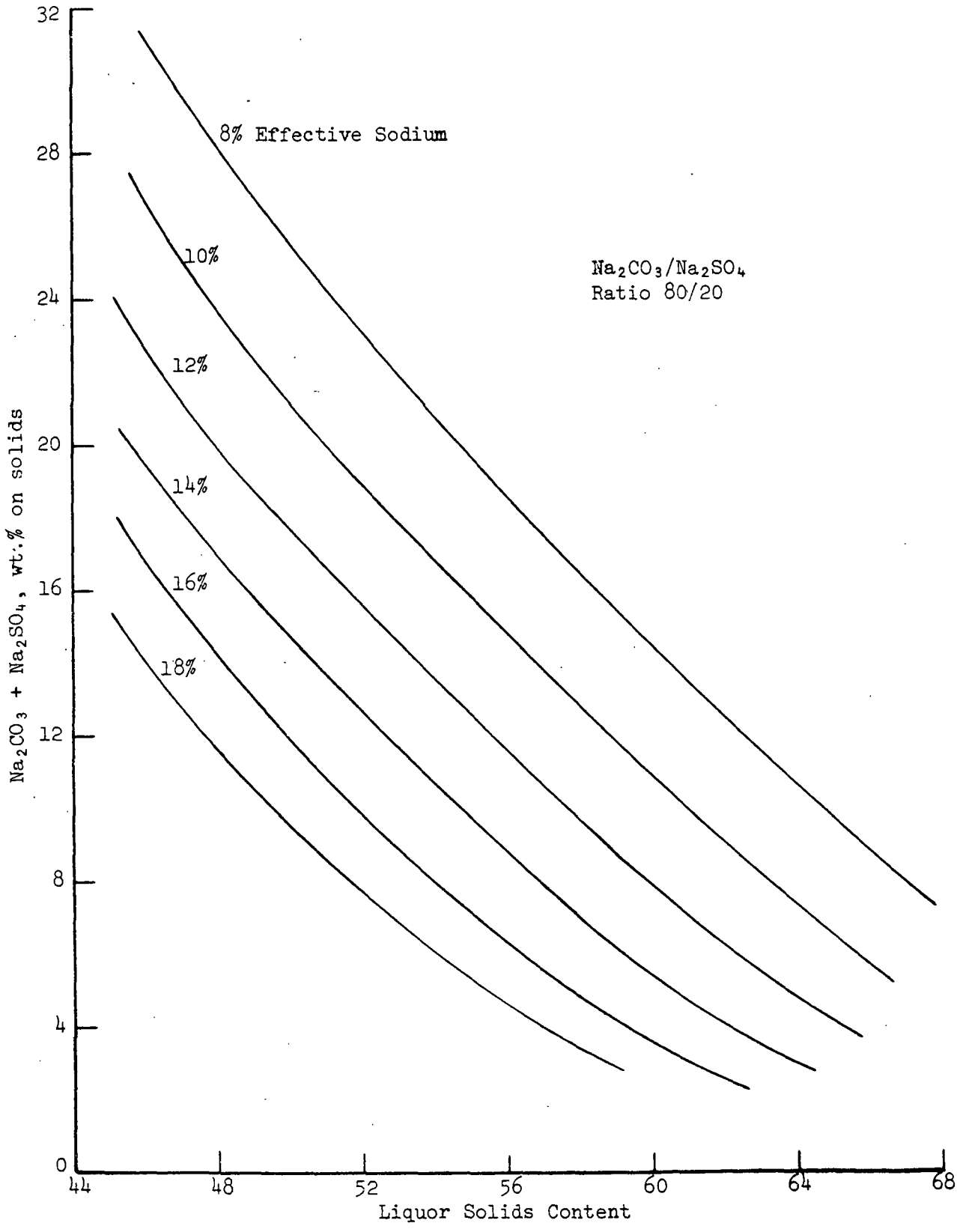

Figure 13. Correlation of Na_2CO_3-Na_2SO_4 Solubility in Black Liquor

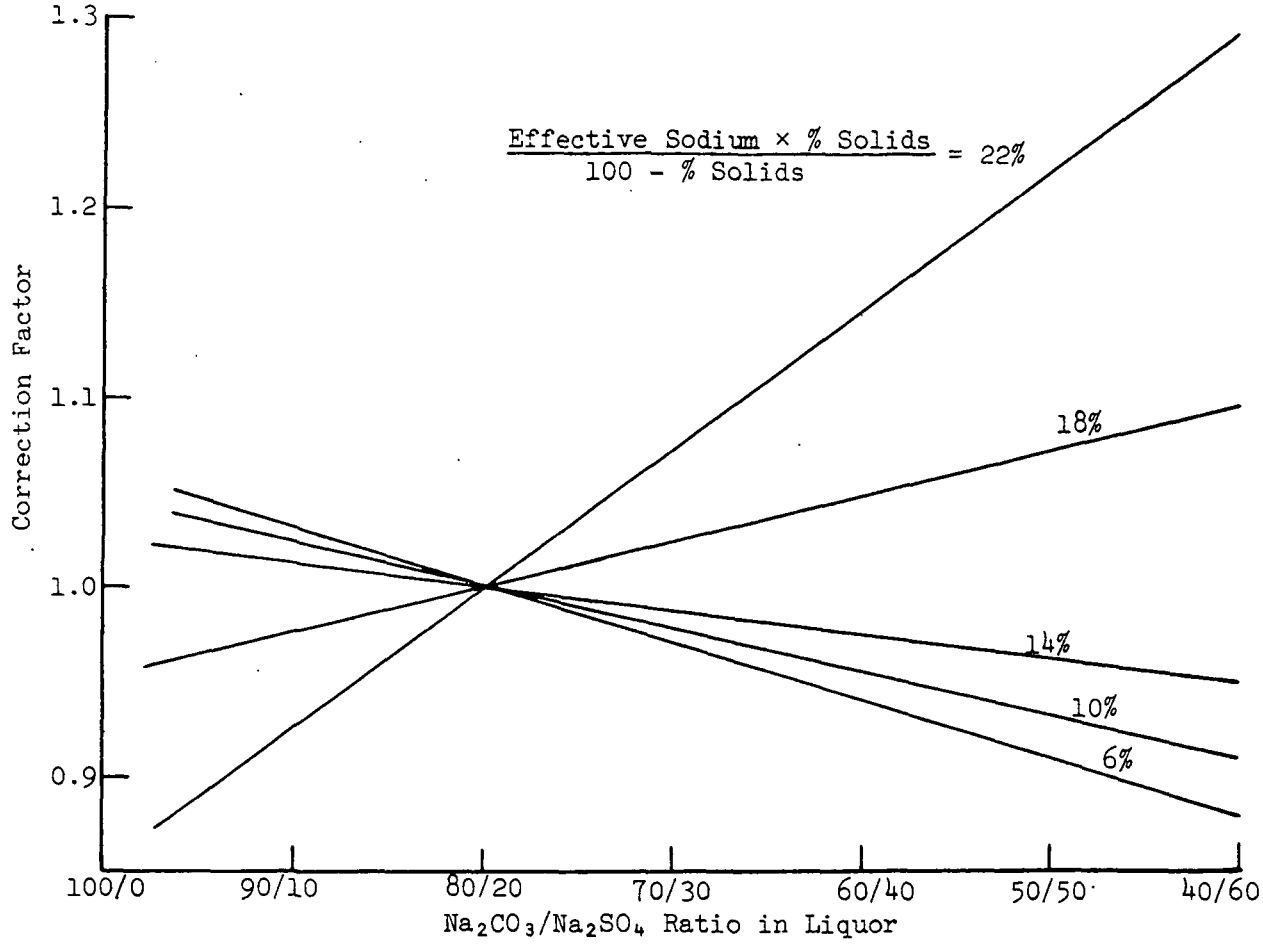

Figure 14. Correction Factor for Na_2CO_3-Na_2SO_4 Solubility to Account for Varying Carbonate/Sulfate Ratios

This latter step is needed because the correction factor is multiplicative for $Na_2CO_3+Na_2SO_4$ [i.e., if Fig. 13 is used to determine the amount of soluble $Na_2CO_3+Na_2SO_4$ at a given solids, the corrected value is $\underline{f} \cdot (Na_2CO_3+Na_2SO_3)_{Fig.\ 13}$].

The degree of saturation at the discharge of the evaporators is calculated from the discharge solids and critical solids as follows:

$$\text{Degree of saturation} = \frac{\left(\frac{1-S}{S}\right)_{critical}}{\left(\frac{1-S}{S}\right)_{discharge}}$$

or

$$\frac{\text{discharge (solids/water)}}{\text{critical (solids/water)}} .$$